Book of Abstracts of the

8th Spring Meeting of the International Society of Electrochemistry

Advances in Corrosion Science for Lifetime Prediction and Sustainability:

A Celebration of the 100th Birthday of Mars Fontana

May 2 to 5, 2010 Columbus, Ohio, USA



International Society of Electrochemistry Rue de Sébeillon 9b 1004 Lausanne Switzerland

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Mars G. Fontana April 4, 1910 – February 29, 1988

Mars Fontana left a legacy that few people could even hope for. He was a scientist, an engineer, an educator, a mentor, an administrator, and a leader. With a handful of others, Fontana brought corrosion into the realm of applied science during the 20th century. His book, Corrosion Engineering, later revised into a new edition with co-author Norbert Greene, was used to teach the subject throughout the world for decades. That book, along with the accomplishments of his students and the generations of young corrosion scientists that followed, cemented the reputation of Fontana and The Ohio State University in the world of corrosion. Roger Staehle, Susan Smialowska, Bob Rapp, and Digby Macdonald each continued the strong tradition of corrosion at OSU. Roger Staehle formally named the Fontana Corrosion Center, which thrives today even as corrosion as a discipline suffers at many universities and laboratories. We deeply feel the honor and responsibility of working at the FCC and carrying on the tradition created and strengthened by our forebears. Regrettably, neither of us ever met Font, though we feel his guiding hand. We are fortunate to have with us many of his former students and colleagues who can still recall his charm and personal fortitude, as will become clear during this meeting. Reproduced below, with kind permission from NACE International, is a tribute to Fontana published in the journal Corrosion shortly after his death. Several of the contributors are here this week, but their words from 1988 are fresh, revealing the connection they felt to their friend and mentor.

We dedicate this conference to the memory and accomplishments of Mars G. Fontana, assured that he would have reveled in the good fortune of his legacy.

Jerry Frankel and Rudy Buchheit Columbus, OH, USA May, 2010

A Tribute

Mars G. Fontana, 77, professor emeritus and former chairperson of metallurgical engineering at the Ohio State University died February 29, 1988 at his home. On that date, the corrosion community lost one of its greatest champions and for many of us who knew him well, we lost a truly great friend. "Font's" personal commitments and priorities need not be reviewed for his colleagues; however, there are others to follow who need to know that men of such dedication have indeed lived and provided the leadership of our society. To provide an indication of the type of man Font really was, a number of his former students, associates, and friends have provided short remembrances of their association with him. He was truly a nice guy who finished first.

Resolutions In Memoriam – Mars G. Fontana

The Ohio State University Board of Trustees

The Board of Trustees of The Ohio State University expresses its deep sorrow upon the death on February 29, 1988, of Mars G. Fontana, former Chairman and Regents' Professor of the Department of Metallurgical Engineering and beloved member of the University family.

In 1927, Mars Fontana was a bright and enthusiastic seventeen-year-old student from the Upper Peninsula, beginning his studies at the University of Michigan. He received his Bachelor's of Science in 1931 and continued graduate study in Chemical Engineering at Michigan. In the Fall of 1934, he had completed his doctoral research and was writing his dissertation. The DuPont Company in Wilmington, Delaware offered him a good position. He accepted and, with the blessing of his Faculty Advisor, Dr. John Chipman, he reported immediately to Dr. Harold Maxwell at DuPont. For the next 53 years, Mars Fontana gave his productive mind, body, and spirit to the advancement of the science and engineering of materials developments and the prevention of corrosion and material failures in engineering systems. The first nine of those years were spent at DuPont, the next thirty at The Ohio State University, and the last fourteen as a senior adviser, writer, and lecturer.

All of us who knew Font as a colleague have many wonderful remembrances of his work and personal dedication. Mars Fontana was really many people. He was a scientist, an engineer, a teacher, a consultant, a leader, a friend, and, most importantly, a loved member of his family. Throughout his career, he received many awards and recognitions for his research and teaching in the fields of corrosion, metallurgy, and materials.

Mars Fontana carefully studied the mechanisms of the interactions of water, harsh chemicals, and stresses on metallic alloys. At DuPont, his science and engineering talents merged as he framed the mechanisms of corrosive attack and designed alloys, inhibitors, coatings, and electrolytic protection systems to prevent failures in production plant systems. These efforts led to his famous definition of The Eight Forms of Corrosion. At The Ohio State University, he created a Corrosion Research Center and organized and led a Department of Metallurgical Engineering that put Ohio State in the forefront of materials research and corrosion science. Dr. Fontana is widely recognized as the Father of Modern Corrosion Science and Engineering. In his role as department chairman, he recruited and nurtured young faculty members, he led efforts to obtain funds for new laboratories, and he took an active part in the administration of the College of Engineering and in the faculty governance of the University. In the latter regard, he served as a member of the Faculty Council and as an effective senior faculty adviser during

many University crises. By the time of his retirement in 1975, he had presented most of the important international lectures in his field and he had been named a Regents' Professor, a member of the National Academy of Engineering, and a Fellow of all the technical societies in his field. In 1981, the Faculty and Board of Trustees officially renamed the building that he had worked so hard to create The Mars G. Fontana Laboratories. Other responsibilities and honors fell on him over the years. He was particularly proud of his honorary doctorate from Michigan and his honorary membership in the American Society for Metals. Just two years ago, he was the first recipient of the Outstanding Educator Award of the Metallurgical Society of AIME.

Mars Fontana, the teacher, changed the lives of all the students in his classes. He emphasized good analysis, clear and concise presentations, and simplicity wherever possible. In his consulting work and later industrial leadership as a director at Worthington Industries, he was famous for his ability to find the key to a complex problem, to identify the critical concerns, and to propose practical and successful courses of action. He passed that on to his students during his entire teaching career. His book, used throughout the world as the definitive engineering textbook on corrosion, emphasizes clear thinking and conciseness.

In Mars Fontana's life, responding to a sophomore student with a question was just as important as meeting a visiting dignitary. He was always open to questions and new ideas. He was very accessible and available to young people. He treated everyone with respect. He was generous with his own funds in many ways. Quietly he helped students and friends over rough spots. His generosity, along with that of his colleagues, friends, and family, led to the endowment of the Mars G. Fontana Professorship. Earlier, a scholarship fund was created in his name.

The Department of Metallurgical Engineering and the Fontana Corrosion Center at The Ohio State University, its faculty, and its students are deeply indebted to his creative efforts. All of the companies for whom he consulted and the men and women who run them were enriched by the advice of Mars Fontana. The quality of public higher education is better because of his dedication to the pursuit of excellence in teaching, research, and public service.

On behalf of the University, the Board of Trustees wishes to express its deep sympathy to Mars Fontana's wife, Betty, and his children, Martha, Mary, Elizabeth, David, and Thomas, their spouses, his beloved grandchildren, and his brother and sister.

R.W. Staehle

Consultant

In his professional life, Font had three major commitments. First, he was committed to being unfailingly courteous. I never heard him say it, but it was always clear to me that the maxim "what you are speaks so loud I can't hear what you say" was the cornerstone of his personal code.

Second, he was committed to teaching students so they would learn. From his insistence on student's writing papers in his classes to his relating personal experiences as virtual engineering parables, he was determined that students would learn. At Ohio State, he built excellent facilities and attracted an outstanding faculty to assure that the students would be well educated. In his short courses and evening speeches, he was delightfully entertaining while still conveying the corrosion message. No one will forget the roaring responses to his famous lion pictures.

Thirdly, he was committed to connecting science and engineering. He understood the feedback. Engineering problems defined challenging problems for science; science provided usable principles for engineers. He lectured frequently on this subject and committed his personal efforts to assuring the effectiveness of the communication. Codifying corrosion into its eight forms was vintage Fontana. Such a formulation provided scientists and engineers with a common language and common directions.

In the larger perspective, Fontana expanded on his work to connect science and engineering to his efforts to connect the University to the society around it. In Columbus, home of The Ohio State University, he was as well known and liked throughout the city as he was at the University for his good works and his genuine niceness.

Fontana symbolized what is good and what is possible from enlightened academics. His students and grand students today permeate the international technology society. Like Fontana, they too are characterized not only by their hard work and commitment to their profession but by their working to make their own institutions and societies better places.

Fundamentally, Font was a magnificent family man. In his professional life, his students, colleagues, and institutions were family.

R. D. McCright

Lawrence-Livermore Laboratory; Chairman, NACE Publications Committee

Mars Fontana was a very unassuming man, yet he commanded an enormous amount of respect. It was a privilege and an unforgettable experience to have studied at Ohio State University in the Department that he built. Fontana was the Godfather, in the most positive sense of the word, to all of us.

R. M. Lantanision

Department of Materials Science and Engineering, Massachusetts Institute of Technology

I have often been asked how I came to choose corrosion engineering as a career. The answer is surprisingly simple. During my second year as a graduate student at OSU in 1965, Font buttonholed me in the corridor outside his office. He said "Ron, we have a new man on the faculty. His name is Roger Staehle and he has lots of good ideas and money. You're going to like corrosion engineering!" In the words of a well-known TV sportscaster, "the rest is history!" Actually, this was one of the best decisions I never made!

My association with Roger Staehle and Roger's, in turn, with Font, is very special — three generations of Fontana engineers! I will never forget the NACE Banquet in 1972 when Fontana presented me with the Campbell Award. I don't remember his words exactly, but he introduced me as a grad student of Roger's and then quickly added that since Roger was his student, that made me his grandson! He said that with the pride of a father... and grandfather; it was clear in his voice that he was very proud. This was a really moving moment for me and, I think, for him and for those in the audience. I remember responding to his introduction by saying that nothing could have made me happier than to have been presented with the Campbell Award by him. I understand how he felt. Last year, fifteen years later, Pete Searson, one of my gang at MIT, won the Campbell Award. And, this year, Dave Burleigh did it again!!

T. and Y. Kondo

Atomic Energy Research Institute, Japan

My wife and I had a great luck of studying corrosion as graduate students at The Ohio State University back in 1962 to 1965, where Professors Fontana and Beck were our advisors. Among many pleasant memories of the days spent under the fine research-humane climates, we particularly appreciate those on the class room activities in the Advanced Corrosion course conducted by Professor Fontana. In the classes, much time was spent on the presentations and discussions on the extensive literature surveys of the various subjects assigned to each student. He was generally very quiet and gave minimum comments and suggestions, which were very essential. In this way, he stimulated his students to extend their own thinking to more creative directions. So many world-known corrosionists have been thus raised.

J. H. Payer

Professor of Materials Science, Case Western Reserve University

From helping this second-year transfer student at OSU find a summer job more than 25 years ago and throughout my career, Dr. Fontana was always available to listen and provide sound counsel. Mars Fontana continued to open doors of opportunity and to expand the horizons of my goals and achievements. He instilled in many of us a curiosity and conviction to understand and solve corrosion problems.

Mars built esprit de corps in many ways, from studentfaculty golf outings to stories from far off lands, e.g., the leisure activities of the king of beasts. An annual testimony to Font's impact and success is the Buckeye Party at the NACE Conference. Mars and Betty would proudly reside over the festivities and glow with satisfaction at good news from around the world.

Many of us are thankful to Mars for help he gave in his personal, quiet way. His special gift was to make each of us feel special.

D. D. Macdonald

Director, Chemistry Laboratory, SRI International

Mars was one of the founders of modern corrosion science and engineering. His contributions to the development of these disciplines was enormous and perceptive, including the education of students, directing of research, and transferring technology to the field. His establishing and nurturing of the corrosion program at Ohio State University provided that university with a world-class center. The impact that the FONTANA Corrosion Center has had on science and technology was amply demonstrated at CORROSION/88, when fifty present or former associates in the FCC, including two past directors, assembled for dinner to pay tribute to Mars. He was acclaimed universally as a gentleman and a scholar, whose memory will live on through the disciplines he helped form, corrosion science and engineering.

H.P.Godard

Aluminum Company of Canada; Former Editor of Materials Performance

I was somewhat of a late comer on the North American corrosion scene, being engaged by Alcan to be their corrosion expert only in 1945. By this time, Fontana, LaQue, Speller, Hackerman, Compton, Mears, Larrabee, Ivy Parker, Wachter, Tracy, Whitney, Boyd, and many others were already well established. Of course, even before them were Speller and Whitney. There were of course many others. I entered the field of corrosion completely "cold," with absolutely no knowledge of corrosion and an equal background in aluminum.

I was less of a newcomer to NACE, which I joined in 1941 when I attended the 3rd annual meeting in Chicago, where the attendance was 631 (at least by my records). Realizing my deficiencies, I sought to broaden my knowledge and establish a number of corrosion "contacts." I arrived in Chicago with a list of desirable contacts I had gleamed from Corrosion magazine and brashly invited them to breakfast, lunch, or dinner just to get acquainted. This way, I met people like Fontana, LaQue, Brannon, Fair, Hackerman, Holcombe, Humble, Munger, Noppel, Olson, Van de Bogart, and others, not only in Chicago, but at later NACE meetings which I attended annually; maybe I even met Boyd this way, but I don't keep a diary which could now refresh my memory.

It wasn't long before I sought out Fontana, and found him only too willing to help a newcomer. His wife Betty was equally friendly and we had a long association of pleasant visits at corrosion affairs over the years. My activities on the Abstract Committee chaired by Ivy Parker put me in even closer contact. Then there was the fateful committee selected to review the editorship for both Corrosion and MP, of which I was a member. We decided to ask Mars to step down for someone with more time and it was my job to try and make peace with Fontana. That experience really taught me the gentleman that he was, for our discussions then and later were always calm and friendly, even when I told him that I had voted for the change, and was probably most responsible for it. We remained close, and to prove it, when many years later I got an invitation to give corrosion lectures in South Africa, the first person I called to ask about South African experience was Mars, as he had been a similar lecturer some years before. His helpful advice contributed greatly to my enjoyment of this pleasant visit.

When I joined the "inner circle" of NACE officers as Vice President in 1958, I began seeing more of Mars and Betty at NACE executive functions, associations that continued until 1983 when I resigned as editor of MP, and dropped from sight in NACE.

Mars was, of course, an undisputed corrosion authority, a warm friendly person beneath his sober mask, and ever willing to help anyone who approached him (which I did countless times over the years). I join all in the corrosion community who knew him personally to mourn his passing. Mars was a corrosion stalwart who will long be remembered. I will drink a silent toast to his memory – Well done, Mars. We will miss you.

H. W. Pickering

Department of Materials Science and Engineering, Pennsylvania State University

Font once invited me to travel with him and his lovely wife Betty to Philadelphia for an ASM meeting. He said he was driving because it was such a beautiful ride through Pennsylvania that time of year when the fall foliage would be displayed in deep reds, bright yellows, and browns. From his comment, I had the impression that Pennsylvania was some place special and I guess the impression stuck. In any case, what I remember best was not the meeting itself but rather the drive through Pennsylvania with Font and Betty. It is probably a coincidence that I have lived in Pennsylvania since those OSU days but, then again, maybe not.

All memories are now fond ones, but I remember one that was hardly pleasant at the time. Font, too, wasn't very happy. He gave me that famous look of his. He thought I was ready for the comprehensive exam and I probably was but the oral part of the exam proved to be somewhat of a problem. The outside member of the committee was from the Chemistry

Department and an expert on x-ray diffraction and its application to microstructural analysis. He began the questioning and revealed some weakness on my part. Afterwards, I wondered how much Font had to do with my passing that exam. I doubt that anyone else remembers that event over 25 years ago (professors Beck and Hirth were the other committee members), but I sure do and maybe if Font were still with us, he would too.

There are many other fond memories, but I will summarize by saying that I have been fortunate and some of the factors that have contributed to this state of well being include the first and foremost direction Font gave me, a focus in the technologically important corrosion area. For this and his many other inputs, I feel a closeness to my former thesis advisor, Professor Mars G. Fontana, who I will also fondly remember as a friend and highly respected educator.

F. H. Beck

Retired Professor Emeritus, The Ohio State University

During the forty-five years that I was acquainted with Font, I knew him as a friend, as a coworker, as my teacher, as my graduate adviser, and as chairman of the OSU Department of Metallurgical engineering of which I was a member. Regardless of the categories listed, Font always treated me simply as his friend.

Font created an environment in his department at OSU that was conducive to excellence in both teaching and research. I was fortunate and glad for the opportunity to stay at OSU and work with him. It was a rewarding and pleasant experience.

Most engineers are familiar with the Eight Forms of Corrosion. Font frequently showed slides of his other more recently identified and less well-known forms of corrosion. For example, a severely corroded automobile he identified as Automobile Corrosion and a severely corroded bicycle was identified to suffer from bicycle corrosion, etc. Some of you may have seen his slides of the passionate lions. I'm not sure about the type of corrosion they suffered from.

Font always enjoyed melting and pouring metals. On many occasions, we would spend an afternoon preparing heats of experimental alloy steels in a 12-pound induction furnace. We used an iron rod to help introduce alloy additions into the molten charges. Before the rod became hot enough to melt, we would plunge the hot end of the rod into a bucket of water for a brief time and then reinsert the still very hot rod into the molten metal.

One day, when I happened to be passing by the furnace room, there was an explosion from within. Some graduate students said that they stuck an iron rod into a charge of molten metal just like Professor Fontana did and the metal exploded. The difference was that the students used a wet rod.

Being a good teacher, Font always tried to be available to his students for consultation and suggestions concerning their work. From this, he gained the admiration and respect of the many students going through his department.

B. E. Wilde

Department of Metallurgical Engineering, The Ohio State University

I first met Mars Fontana and fell under his spell as a recent graduate from RPI whilst attending a Stress-Corrosion Conference at The Ohio State University in 1967. Although I was familiar with his research and teachings in corrosion science, I was immediately attracted by his rare gift of being able to communicate comfortably and meaningfully with the doers of this world – the engineers.

Over the intervening 21 years, I have come to recognize first hand that Mars G. Fontana was one of the true founding fathers of American Corrosion Engineering who was at home either as an educator or as an industrial problem solver. I am proud to have known him, and to have the on-going privilege of teaching his course in Corrosion engineering in the Department of Metallurgical Engineering that he created at The Ohio State University. I shall miss him.

R.A. Rapp

Department of Metallurgical Engineering, The Ohio State University

On February 29, 1988, Professor Emeritus Mars G. Fontana passed away. At his memorial service, his son David Fontana eulogized his father by starting out "Mars Fontana, he was quite a guy." By comparison with David, my relationship over 25 years with Font as my boss, colleague, friend, and role model was far too brief. But I also knew Font's kindness, fairness, friendliness, guidance, and generosity. I was treated like a son by Mars Fontana. He was one of the nicest gentlemen that I have ever met; how lucky to work with him and exchange thoughts and jokes over those years. How lucky I was to receive encouragement and support from my Department Chairman and the excellent faculty which Font drew to Ohio State University. We all appreciated it, and we all will miss Font.

I have mentioned these personal matters, because Font's professional achievements as a teacher, a researcher, an author, and a consultant are all pretty well known and recognized. Yes, Mars Fontana, he was quite a guy.

New Materials Division, Nippon Steel Corporation, Japan

I often stopped writing this short memoir recalling and traveling the most pleasant and thank worthy memories with Professor Fontana. Whenever we saw him with typical student's problems, he was ready to ease our worries especially on the bitter days after tough exams. A red sports car parked in front of the office, picnics at golf courses, and Park of Roses, students/ faculty banquets which were full of jokes, holidays in Tokyo with his lovely wife, and so on. Those shall remain in our memories. Please be with us forever.

R.C.Clark

Olin Chemicals

In 1976, while I was working on my master's degree, I had the honor of being the grad student who was doing the metallography for Dr. Fontana's failure analysis consulting work. I learned a lot about integrity and ethics, as well as how to conduct a real failure analysis, working for him.

The day I remember best occurred in early summer. I met with him to discuss the progress of a current failure analysis job. However, Dr. Fontana had just returned from an ASTM committee meeting and was upset by the outcome.

He and Duriron had presented some results of an investigation into unexpected corrosion problems with high alloy castings. They covered the problem, the cause of the problem, and the solution of the problem. Other vendors, who constituted a majority on the committee, voted not to incorporate any of the suggested improvements in the applicable ASTM standard. He told me that if they had taken that stand because they disagreed with his experiments or his conclusions, he could have respected them. However, no one disagreed with the presentation. He told me that the majority had voted against changing the ASTM standard to require improved casting quality, because they would have had to buy some new equipment to meet the new requirements. He could not respect them for knowingly voting to block new standards promoting better castings.

I have never forgotten him, his views on right and wrong, and his common sense attitudes.

W. K. Boyd

Consultant

At the time I graduated from Ohio State University, Font was just coming on as chairman of the Department of Metallurgy. I have regretted that I did not have the opportunity to study under Font. However, living in Columbus and working just across the campus at Battelle afforded me a rare opportunity to have Font as both a friend and colleague for more than 40 years. You might say I had the best of two worlds. We played golf together, shared jokes, and withstood the vigors of losing at cribbage to our wives, but, best of all, we were friends. I can't tell you what it means to have a friend like Font.

Each year at the annual NACE convention, Font would take it upon himself to acquaint the ladies with the various facets of corrosion and corrosion prevention. At first, the tour through the exhibits involved only a few ladies; however, as the word got out, it evolved into what became known as Font's Harem. In fact, Font leading a group of ladies through the exhibits became a regular part of the corrosion show. He was in his glory and so were the ladies — just ask any of them what they most remember about the annual meeting.

G. R. St. Pierre

Department of Metallurgical Engineering, The Ohio State University

I was recruited by Font in the Spring of 1956, but I didn't actually start as a regular faculty member until late 1957. My 32 years of association with Font are filled with warm recollections. We played golf and bridge together on many occasions and he was always a gentleman of good spirit. We had the same faculty adviser, John Chipman. Font's PhD degree, with Chipman as adviser, was awarded by the University of Michigan in 1935. In 1954, I received my PhD from MIT, with Chipman as an adviser. Many other coincidences linked us in time and place. Font will always have a special place in my heart beside my Father, John Chipman, and Carl Wagner. Font was the father of modern corrosion science in engineering, but he also influenced many young scientists and engineers throughout the entire field of materials science and engineering.

On behalf of the students, staff, faculty, and alumni of the Department of Metallurgical Engineering, I am pleased to send a special message of our undying love and admiration for Mars G. Fontana.

S. Abe

Yawata Technology Division, Nippon Steel Corporation, Japan

I heard the very sad news of Professor Fontana's death. As I recall, Professor Fontana has planted the fruitful seeds of corrosion scientists and engineers throughout the world. From the heaven, he must be watching those seeds still growing even in Japan.

R. B. Puyear

Monsanto Chemical Company

In 1977, a group of us had just formed the Materials Technology Institute of the Chemical Process Industries, Inc. and were looking for a person to serve as our first Executive Director. When we considered the people who might be available for this part-time job, we immediately thought of Mars Fontana, who had recently retired from The Ohio State University. However, the word was that when Mars retired, he made it clear that he had no interest in working. In addition, we felt that it was a bit presumptuous to ask a man of his stature to take this part-time job at the rather low salary we were able to offer. Nevertheless, we worked up the courage to approach him at the NACE meeting to see if he would be interested in working with us.

This brings me to the point of the story. We interviewed Mars along with several other candidates for the Executive Director job. With the other candidates, the interview went about how you might expect. We outlined the requirements of the job and the candidates explained how they could satisfy these requirements. With Mars, the interview immediately took a different turn. Instead of us interviewing him, he interviewed us to see if we at MTI met his standards and if we were serious about supporting it. It wasn't until the interviews were completed that we realized how completely the tables had been turned. We passed the test; he became our Executive Director!

Mars was in control of the situation! We came to learn that this was one of his characteristics. He had such strength of personality that others instinctively differed to him. His leadership got MTI off to a strong start and helped make it the influential organization that it is today.

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Sunday, May 2, 2010

Lobby of University Plaza Hotel

14:00 to 17:00 Registration

Ohio Student Union

19:00

Welcome Reception sponsored by DNV Shuttle bus from University Plaza Hotel provided starting at 18:30

Monday, May 3, 2010 - Morning

Multi-purpose room

Chair: G. Frankel

08:30 to 09:15 Keynote

Digby Macdonald (*Materials Science and Engineering, Pennsylvania State University, University Park, USA*)

The Early History of Passivity Research at the Fontana Corrosion Center

Coatings I

Multi-purpose room

Chairs: G. Frankel, K.Y. Kim

09:25 to 09:50 Invited

Herman Terryn (Electrochemical and Surface Engineering, Vrije Universiteit Brussels, Brussels, Belgium), Guido Grundmeier, Arjan Mol, Ralf Posner, Peyman Taheri, Jan Wielant

Influence of the Nano Oxide Metal Films on the Interaction with Organic Coatings

09:50 to 10:15 Invited

Michael Rohwerder (*Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany*)

Application of Conducting Polymers for the Corrosion Protection of Iron and Zinc

10:15 to 10:40

Brian Hinderliter (*Coatings and Polymeric Materials, North Dakota State University, Fargo, USA*)

Simulation of Electromagnetic Response (EIS) of Corrosion Protective Coatings to Flaws

10:40 to 10:55

Coffee Break

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10:55 to 11:20

H. Tsaprailis (DNV Columbus, Materials and Corrosion Technology Center, Dublin, USA), H. Cong, Luis Garfias

A Novel Method to Measure In-situ Corrosion and Degradation **Reactions Occurring inside Pressurized Aerosol Containers**

11:20 to 11:45

Vinod Upadhyay (Coatings and Polymeric Materials, North Dakota State University, Fargo, USA), Kerry Allahar, Gordon Bierwagen

Environmental humidity influence on a topcoat/Mg-rich primer system with embedded electrodes

11:45 to 12:10

Sergej Toews (Universität Paderborn, Coating and Surface Technology, Paderborn, Germany), Wolfgang Bremser

Smart Functionalized Polymer Dispersions for Effective Mapping of Heterogeneous Metal Surfaces: New Concepts for Corrosion Protection

Iron and Nickel Alloys I

International Hall

Chairs: R. Buchheit, P. Andresen

09:25 to 09:50 Invited

Roger Newman (University of Toronto, Dept. of Chemical Engineering and Applied Chemistry, Toronto, Canada), Gregmar Chirinos, Andrew Garner Science-Based Maps and Correlations for Stainless Steel

09:50 to 10:15 Invited

Kyoo Young Kim (Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang, Korea), Jeong Kil Kim, Yeong Ho Kim

New Findings on Intergranular Corrosion Mechanism of Ti-stabilized Ferritic Stainless Steels

10:15 to 10:40

Bruno Vuillemin (ICB, Interfacial Electrochemistry Corrosion Group, Dijon, France), Roland Oltra, Aurelien Percheron

Study of Crevice Corrosion by Coupling pH Measurements by TIRFM with FEM Modeling

10:40 to 10:55

Coffee Break

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8th Spring Meeting of the International Society of Electrochemistry

10:55 to 11:20 page 77 Jae-Bong Lee (School of Advanced Materials Engineering, Kookmin University,

Seoul, Korea), Jae-Jung Kim, Kyu-Seop Kim

Studies on Corrosion Characteristics of Fe-Cr Alloys and Sensitized STS 304 Using the Micro-droplet Cell Technique

11:20 to 11:45

Hyuk Sang Kwon (Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, DaeJeon, Korea), Kyung Jin Park

Effects of Mn on the Localized Corrosion Behavior of Fe-18Cr Alloys

11:45 to 12:10

Yeong Ho Kim (*POSCO Technical Research Lab.*, *Pohang, Korea*)

Life Prediction and Field Corrosion Behavior of Stainless Steel for Automotive Mufflers

High Temperature I

Eastman Hall

Chairs: R. Rapp, J. Smialek

09:25 to 09:50 Invited

Peter Tortorelli (Oak Ridge National Laboratory, Oak Ridge, USA), Michael Brady

Turning Corrosion Around: Using High-Temperature Oxidation Principles for Synthesis of Functional Materials and Application to PEM Fuel Cell Bipolar Plates

09:50 to 10:15

Robert Rapp (Department of Materials Science and Engineering, The Ohio State University, Columbus, USA)

The Role of the Metal/Scale Interface in the Growth of Protective Scales on Metals

10:15 to 10:40

R.C. John (*CRCT*, *Ecole Polytechnique de Montréal, Montreal, Canada*), A.D. Pelton, W. T. Thompson, I.G. Wright, A.L. Young

Managing High Temperature Corrosion in the 21st Century

10:40 to 10:55

Coffee Break

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10:55 to 11:20

page 103

Bruce Pint (Oak Ridge National Laboratory, Oak Ridge, USA)

Quantifying Degradation Mechanisms of Alumina-Forming Alloys for Energy-Related Applications

11:20 to 11:45

page 126

Peter Tortorelli (Oak Ridge National Laboratory, Oak Ridge, USA), Michael Brady

High-Temperature Sulfidation of Alumina-Forming Alloys

11:45 to 12:10

page 132

Kinga A. Unocic (Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, USA), Michael P. Brady, Bruce A. Pint

The Oxidation Behavior of Commercial Alumina-Forming Austenitic Steel

Monday, May 3, 2010 - Afternoon

Multi-purpose room

Chair: R. Buchheit

13:15 to 14:00 Keynote

Roger Staehle (Staehle Consulting, North Oaks, USA)

The "Wedging Action" of Compounds as a Damage Process Important to Professor Fontana

Coatings II

Multi-purpose room

Chairs: M. Rohwerder, W.T. Tsai

14:10 to 14:35

Herman Terryn (Vrije Universiteit Brussels, Group of Electrochemical and Surface Engineering, Brussels, Belgium), Iris De Graeve, Annick Hubin, Jean-Baptist Jorcin, Gill Scheltjens, Els Tourwé, Guy Van Assche, Yves Van Ingelhem, Bruno Van Mele

A Coating Combination of Self-Healing Polymers and Corrosion Inhibitors for Active Corrosion Protection of Metals

14:35 to 15:00

Santiago Garcia Espallargas (Department of Aerospace Materials and Manufacturing, Delft University of Technology, Delft, Netherlands), H.R. Fischer, A.E. Hughes, J. Mardel, J. M. C. Mol, P.A. White

Self-Healing Anticorrosive Organic Coating Based on the Release of a Reactive Silyl Ester

15:00 to 15:25

Ralf Posner (Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), Stephan Amthor, Guido Grundmeier, Martin Marazita, Konrad J. Roschmann, Kristof Wapner

The polymer network structure as a key parameter for the corrosion resistance of polymer/oxide/metal interfaces

15:25 to 15:40

Coffee Break

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15:40 to 16:05

Douglas Hansen (University of Dayton Research Institute, Dayton, USA), Karolyn Hansen, Andrew Mount, Yuhchae Yoon

Electrochemical Characterization of Oyster Shell as an Environmentally Friendly Ceramic Coating Material

16:05 to 16:30

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page 117

Xuecheng Dong (Dept. of Chemical and Materials Engineering, Univ. of Cincinnati, Cincinnati, USA), Dale W. Schaefer

In Situ Evolution of Non-Chromate Inhibitor Films by Simultaneous Neutron Reflectivity and Electrochemical Methods

16:30 to 16:55

page 39

Saikat Adhikari (Fontana Corrosion Center, The Ohio State University, Columbus, USA), G. S. Frankel, Kinga A. Unocic, Yumei Zhai

Hexafluorozirconic Acid Based Surface Pretreatments as a Replacement for Phosphate Conversion Coating: Characterization and Performance Assessment

Iron and Nickel Alloys II

International Hall

Chairs: M. Stratmann, J. Noel

14:10 to 14:35

Vincent Vignal (ICB, CNRS-Univ. Bourgogne, Dijon, France), Hassan Amar, Olivier Heintz, Halina Krawiec, Dominique Mainy, Jerome Peultier, Vincent Vignal

Passive properties of duplex stainless steels after long-time ageing in air studied using EBSD, local electrochemical impedance spectroscopy, XPS and Auger

14:35 to 15:00

Dmitrij Zagidulin (Department of Chemistry, University of Western Ontario, London, Canada), Pellumb Jakupi, James J. Noël, David W. Shoesmith, Xiangrong Zhang

Structure and Composition of an Alloy 22 Surface Preoxidized at Different Conditions.

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15:00 to 15:25

Namurata Sathirachinda (Div. of Surface and Corrosion Science, School of Chemical Science and Engineering, Royal Institute of Technology, KTH, Stockholm, Sweden), Jinshan Pan, Rachel Pettersson, Sten Wessman

SEM/EDS and SKPFM Study of Chromium Nitrides in Duplex Stainless Steels - Limitations and Implications

15:25 to 15:40

Coffee Break

15:40 to 16:05 Invited

Howard W. Pickering (Department of Materials Science and Engineering, The Pennsylvania State University, University Park, USA), Faisal M. Al-Faqeer, Hung-Kai Shu

Initial Passive Film Breakdown on Crevice Wall for Iron in Near Neutral Sulfate Chromate Solution

16:05 to 16:30

Koji Fushimi (Graduate School of Engineering, Hokkaido University, Sapporo, Japan), Hiroki Habazaki, Hidetaka Konno, Masahiro Seo, Takatoshi Yamamoto Mechano-electrochemistry of Passive Surface Using In-situ Microindentation Test

16:30 to 16:55

Gerald Frankel (Fontana Corrosion Center, Ohio State Univ., Columbus, USA), Michael Stevenson

Investigation into the Corrosion of Steel under or near Grease Layers

SCC

Eastman Hall

Chairs: R. Staehle, E.H. Han

14:10 to 14:35 Invited

Peter Andresen (GE Global Research Center, Schenectady, USA)

Perspective on SCC Response and Prediction in Nuclear Power System

14:35 to 15:00

Digby Macdonald (Materials Science and Engineering, Pennsylvania State University, University Park, USA)

The Electrochemistry of Stress Corrosion Cracking

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15:00 to 15:25 Invited

En-Hou Han (Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China), Jianqiu Wang

Crack Initiation on Alloy 690 in Lead-Contaminated High Temperature Pressurized Water

15:25 to 15:40

Coffee Break

15:40 to 16:05

Jingli Luo (Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Canada), Bao-Tong Lu, Yu-Cheng Lu, Lian-Peng Tian, Ren-Kang Zhu

Investigation of Stress Corrosion Cracking of Alloy 800 in Neutral Crevice Solutions

16:05 to 16:30

Eiji Akiyama (National Institute for Materials Science, Tsukuba, Japan), Songjie Li, Tadashi Shinohara, Kaneaki Tsuzaki, Zuogui Zhang

Evaluation of Hydrogen Embrittlement Property of High Strength Steels

16:30 to 16:55

Xiaoyuan Lou (School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, USA), Preet Singh

Local Passivation Breakdown of Carbon Steel in Bio-ethanol during Stress Corrosion Cracking

First poster session in the late afternoon with a reception

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Tuesday, May 4, 2010 - Morning

Multi-purpose room

Chair: G. Frankel

08:30 to 19:15 Keynote

page 32

Ivan Cole (CSIRO, Clayton, Australia), Emmanuel Bosco, Gunasegaram Dayalan, Venkatraman Murali, Muster Tim

Multi-Scale Modeling of Atmospheric Corrosion

Coatings III

Multi-purpose room

Chairs: H. Terryn, D. Hansen

09:25 to 09:50

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R.G. Buchheit (Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), F. Gambina

Characterizing the Relationship between EIS Measurements and Exposure Testing Results Using Neural Networks and Fuzzy Set Theory

09:50 to 10:15

Bruno Vuillemin (ICB, Interfacial Electrochemistry Corrosion Group, Dijon, France), Christian Allely, Kevin Ogle, Roland Oltra, Florian Thebault

Experimental Evidence of the Inhibition of the Oxygen Reduction on Galvanized Steel Cut-Edges

10:15 to 10:40 Invited

Luis F. P. Dick (*Depto. de Metalurgia, Porto Alegre, Brazil*), Joel S. Rodrigues SVET-Study of the Electrochemical Behavior of Different Hot-Dip Zn-Based Coatings on Steel

10:40 to 10:55

Coffee Break

10:55 to 11:20

Elif Alyamac (Department of Polymer Engineering, The University of Akron, Akron, USA), Rudolph G. Buchheit, Hua Gu, Shuyan Qiu, Mark D. Soucek

Alkoxysilane Oligomer Modified Epoxide Primers for Automotive Coatings

Program

11:20 to 11:45

C.F. Oduoza (School of Engineering and Built Environment, University of Wolverhampton, City Campus, United Kingdom), M.E Khan

Nickel Undercoat to Improve Chromium Electrodeposition of Aluminium Alloys

11:45 to 12:10

Rajendran Nallayan (Department of Chemistry, Anna University Chennai, Chennai, India), Muthiurlan Paandi

Conducting Polymer- Silica Nanoparticles Based Hybrid Nanocomposites: A Facile and Green Synthetic Approach for Active Anti Corrosive Coatings

12:10 to 12:35

Maozhong An (Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, China), Chongxing Li, Jinqiu Zhang

Study of chromium-free passivation process of Ti-P-Si-Mo compound system for electrogalvanized coating

Concrete and Atmospheric Corrosion

Boardroom

Chairs: F. Mansfeld, I. Cole

09:25 to 09:50 Invited

Changjian Lin (State Key Lab of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, China), Shigang Dong, Ronggui Du, Ronggang Hu

A Multifunctional Sensor for *In-situ* Monitoring Corrosion of Steel Reinforced Concrete Structure

09:50 to 10:15 Invited

Carmen Andrade (Eduardo Torroja Institute, CSIC, Madrid, Spain), Isabel Martinez

Non-Contacting Method for the Corrosion Rate Measurement in Concrete Structures: Study about the Correct Electrical Model to be Applied

10:15 to 10:40

Luciano Lazzari (Politecnico di Milano Dipartimento di Chimica Materiali Ingegneria Chimica, Milan, Italy), Luca Bertolini, Fabio Bolzoni, Tommaso Pastore

Pietro Pedeferri's Great Contribution on Understanding Corrosion in Concrete

Program

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10:40 to 10:55

Coffee Break

10:55 to 11:20

Tim Muster (CSIRO Materials Science & Engineering, Clayton, Australia), Avi Bendavid, Angela Bradbury, Svetlana Dligatch, Deborah Lau, Tracey Markley, Phil Martin, Adrian Trinchi

The effects of droplet-surface interactions on the atmospheric corrosion of zinc

11:20 to 11:45

Qiaoxia Li (Department of Material Science and Engineering, University of Virginia, Charlottesville, USA), William C. Keene, Robert G. Kelly, John R. Maben

Chemical Characteristics of Material Surfaces Exposed to Ambient **Coastal Marine Atmospheres**

11:45 to 12:10

Erica Neiser (Center for Electrochemical Science and Engineering, Department of Materials Science, University of Virginia, Charlottesville, USA), Rob Kelly

Atmospheric Corrosion of Silver and Its Relation to Accelerated Testing

12:10 to 12:35

Eric Schindelholz (University of Virginia, Materials Science and Engineering, Charlottesville, USA), Robert G. Kelly

Application of Inkjet Printing for Salt Deposition Prior to Atmospheric **Corrosion Testing**

High Temperature II

Eastman Hall

Chairs: E. Opila, R. John

09:25 to 09:50

Vilupanur Ravi (Chemical and Materials Engineering, California State Polytechnic University, Pomona, USA), Richard Kaner, Jordan Koch, Christian Kouttjie, Andrew Lech, Thuan Nguyen

Engineered Coatings Using Pack Cementation Processes

09:50 to 10:15

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Bruce Pint (Oak Ridge National Laboratory, Oak Ridge, USA)

Development and Performance of Al-Rich Oxidation Resistant Coatings for Fe-Base Alloys

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10:15 to 10:40 Invited

Vilupanur Ravi (Chemical and Materials Engineering, California State Polytechnic University, Pomona, USA), T. D. Claar

Materials for High Temperature Thermal Shock Applications

10:40 to 10:55

Coffee Break

10:55 to 11:20 Invited

Gerald Meier (Univ. of Pittsburgh, Pittsburgh, USA), Frederick Pettit The Effects of Water Vapor and Hydrogen on the High-Temperature Oxidation of Alloys

11:20 to 11:45

James Smialek (Materials and Structures, NASA Glenn Research Center, Cleveland, USA)

Moisture-Induced Alumina Scale Spallation: The Hydrogen Factor

11:45 to 12:10

Brett Tossey (DNV Columbus, Inc., Dublin, USA), Tom Andress, Hassan Khan, The effect of cold work due to shot peening on the steam oxidation resistance of Type 304H austenitic stainless steel

Light Metals I, Ti/Mg/Si

International Hall

Chairs: N. Birbilis, K. Ogle

09:25	to	09:50
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James Noel (Dept. of Chemistry, The University of Western Ontario, London, Canada), David Shoesmith, Li Yan

The Role of Proton Reduction in Complicating the Crevice Corrosion of Titanium

09:50 to 10:15 Invited

Wen-Ta Tsai (Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan), Jhen-Rong Chen, Wan-Shan Kang, Wen-Ta Tsai

In Situ Corrosion Monitoring of Ti-6Al-4V Alloy in H_2SO_4 /HCl Mixed Solution Using ECAFM

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Program

Tuesday, May 4, 2010 - Morning

10:15 to 10:40

Masatoshi Sakairi (Graduate School of Engineering, Hokkaido University, Sappro, Japan), Tatsuya Kikuchi, Misaki Kinjyo

Repassivation Behavior of Ti in Artificial Saliva with PRM

10:40 to 10:55

Coffee Break

10:55 to 11:20

Maria Pia Pedeferri (Politecnico di Milano, Dipartimento di Chimica Materiali Ingegneria Chimica, Milan, Italy), Andrea Brenna, Maria Vittoria Diamanti, Marco Ormellese

Pitting-Induced Surface Alteration of Titanium

11:20 to 11:45

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Geraint Williams (Swansea University, Swansea, United Kingdom), Richard Grace, Neil McMurray

Chloride-Induced Filiform Corrosion of Magnesium

11:45 to 12:10

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Daming Gu (Department of Chemistry, Harbin Institute of Technology, Harbin, China), Maozhong An, Xinghua Guo

Preparation of anodization/SNAP film coated on magnesium alloy and study of its corrosion protection

12:10 to 12:35

page 85

Abdel Salam Makhlouf (Max-Planck-Institute of Colloids and Interfaces, Potsdam, Germany), Darryl Butt, Mahmoud Farahat, Brian Marx

Self-Healing Coatings for Magnesium Alloys

Second poster session after lunch

Excursion in the afternoon

Banquet at the OSU Main Library starting at 18:30

Wednesday, May 5, 2010 - Morning

Multi-purpose room

Chair: R. Buchheit

08:30 to 09:15 Keynote

page 34

Philippe Marcus (*Physical Chemistry of Surfaces, CNRS-Chimie ParisTech, Paris, France*), Boubakar Diawara, Philippe Marcus, Vincent Maurice

Passivity and Passivity Breakdown: a Combined Experimental and Atomistic Modeling Approach

09:15 to 09:30

Coffee Break

Modeling

International Hall

Chairs: R. Newman, C. Andrade

09:25 to 09:50

Nicolas Murer (The Ohio State University, Fontana Corrosion Center, Columbus, USA), Rudolph Buchheit

Stochastic Modeling of Pitting Corrosion in Aluminum Alloys

09:50 to 10:15

Barry Hindin (Battelle Memorial Institute, Columbus, USA), Homero Castaneda, Ayako Yajima

A proposed model for coated steel exposed to simulated soil environments by integrating mechanistic and statistical approaches

10:15 to 10:40

Kiran Deshpande (GM Technical Centre India Pvt Ltd, Bangalore, India) Modeling of Micro-Galvanic Corrosion

10:40 to 10:55

Coffee Break

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10:55 to 11:20 page 45 Francois Ayello (Det Norske Veritas Research & Innovation, Dublín, USA), Pablo Cincunegui, Davion Hill, Stefan Marion, Narasi Sridhar

Integrated Sensor Networks for Corrosion Under Insulation: Monitoring, Cost Reduction, and Life Extension Strategies Part 1: Monitoring -Detection of Cui

11:20 to 11:45

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page 101

Mary Cavanaugh (The Ohio State University, Columbus, USA), Nick Birbilis, **Rudy Buchheit**

Neural Network Modeling of Pit Growth Kinetics in Aluminum Alloys

11:45 to 12:10

Joe H. Payer (University of Akron, Akron, USA)

Advances in Corrosion Science for Greater Safety, Reliability and Performance

Light Metals II, Al

Multi-purpose room

Chairs: D. Macdonald, C. Lin

09:25 to 09:50

Nick Birbilis (Department of Materials Engineering, Monash University, Clayton, Australia)

Use of electrochemical atomic force microscopy to understand the localised corrosion of light metals

09:50 to 10:15 Invited

Kurt Hebert (Department of Chemical & Biological Engineering, Iowa State University, Ames, USA), Jiahe Ai, Gery Stafford, Guiping Zhang

Formation of Localized Corrosion-Relevant Surface Defects on Aluminum - Experimental Studies and Kinetic Monte Carlo Simulation

10:15 to 10:40 Invited

Florian Mansfeld (Mork Family Department of Chemical Engineering and Materials Science, USC Viterbi School of Engineering, University of Southern California, Los Angeles, USA), John Daugherty, Yuelong Huang, Florian Mansfeld, Hong Shih The Corrosion Resistance of Anodized Aluminum 6061 during Long-

Term Exposure and after a Thermal Cycling Treatment

10:40 to 10:55

Coffee Break

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10:55 to 11:20 Invited

Kevin Ogle (Physical Chemistry of Surfaces, UMR7045, Ecole Nationale Supérieure de Chimie de Paris, Paris Tech, France), Polina Volovitch, Meriem Mokaddem, Roland Oltra, Fabien Rechou

The Anodic and Cathodic Dissolution of Al Alloys by Atomic Emission Spectroelectrochemistry

11:20 to 11:45

Kevin Ralston (ARC Centre of Excellence for Design in Light Metals, Department of Materials Engineering, Monash University, Clayton, Australia), Nick Birbilis

Effect of Grain Size and Processing on the Corrosion Resistance of Aluminium

11:45 to 12:10

Mara Shedd (Center for Electrochemical Science and Engineering, Department of Materials Science and Engineering, University of Virginia, Charlottesville, USA), Robert Kelly

Development of an Electrochemical Method of Detection of Sensitization in Al-Mg Alloys

High Temperature III

Boardroom

Chairs: P. Tortorelli, G. Meier

09:25 to 09:50

Elizabeth Opila (NASA Glenn Research Center, Cleveland, USA), Meredith Boyd Oxidation of SiC fiber-reinforced SiC matrix composites with a BN interphase

09:50 to 10:15

T.A. Parthasarathy (*Materials and Manufacturing Directorate, AFRL/MLLN, Wright-Patterson AFB, USA*), R.J. Kerans, M. Opeka, R.A. Rapp

A Model for predicting oxidation kinetics of refractory diborides

10:15 to 10:40

Dongming Zhu (*NASA Glenn Research Center, Cleveland, USA*), Robert A. Miller, James L. Smialek

Ionic Transport and Durability of Advanced Thermal Barrier Coatings

10:40 to 10:55

Coffee Break

Program

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8th Spring Meeting of the International Society of Electrochemistry

10:55 to 11:20

page 107

Robert Rapp (Department of Materials Science & Engineering, The Ohio State University, Columbus, USA)

The Role of Chromium in the Hot Corrosion of Metals

11:20 to 11:45

page 142

Tian Zhongliang (School of Metallurgical Science and Engineering, Changsha, China), Yuan changfu, Li Jie, Lai Yanqing

Corrosive Resistance of NiFe2O4 Based Cermet Inert Anodes in Low Temperature Electrolyte Na₃AlF₆-K₃AlF₆-AlF₃ for Aluminum Electrolysis

Oil/Gas/Pipeline Corrosion I

Eastman Hall

Chairs: M. Orazem, M. Iannuzzi

09:25 to 09:50

Srdjan Nesic (Institute for Corrosion and Multiphase Flow Technology, Ohio University, Athens, USA)

Causes and mechanisms of localized CO₂ corrosion

09:50 to 10:15

Raymundo Case (Production Assurance Technology (PAT), Bartlesville Technology Center, Bartlesville, USA), Raymundo Case, Sudhakar Mahajanam, Dale McIntyre, Hernan Rincon

Effect of Intermetallic Content on the Pit Stability and Propagation Kinetics of Duplex Stainless Steel Exposed to CO₂ Saturated Production Brine

10:15 to 10:40

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Hui Li (Institute for Corrosion and Multiphase Technology, Department of Chemical and Biomolecular Engineering, Ohio University, Athens, USA), Bruce Brown, Srdjan Nesic

A Mechanistic Model of Localized CO₂ Corrosion for Carbon Steel

10:40 to 10:55

Coffee Break

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10:55 to 11:20

Jin Huang (Institute for Corrosion and Multiphase Technology, Department of Chemical and Biomolecular Engineering, Ohio University, Athens, USA), Bruce Brown, Brian Kinsella, Srdjan Nesic

Application of Electrochemical Impedance Spectroscopy for the Study of Under Deposit CO₂ Corrosion of Mild Steel

11:20 to 11:45

Lei Huang (Institute for Corrosion and Multiphase Technology, Department of Chemical and Biomolecular Engineering, Ohio University, Athens, USA), Bruce Brown, Srdjan Nesic

Investigation of Environmental Effects on Intrinsic and Galvanic Corrosion of Welded Carbon Steel in CO₂ Environments

11:45 to 12:10

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page 67

Seth Silverman (Hess Corporation, Houston, USA)

Failure and Reliability Issues of Equipment in a Large Natural Gas Liquids Processing Plant

Wednesday, May 5, 2010 - Afternoon

Multi-purpose room

Chair: G. Frankel

13:15 to 14:00 Keynote

Martin Stratmann (*Max-Planck-Institut für Eisenforschung, Duesseldorf, Germany*) Novel Approaches to an Old Problem: Selective Dissolution of Binary Alloys

Cu

International Hall

Chairs: K. Hebert, B. Hindin

14:10 to 14:35

Yves Van Ingelgem (SURF Vrije Universiteit Brussels, Brussels, Belgium), Annick Hubin

Modeling the fast initial stages of copper corrosion using multisine EIS combined with supporting experimental techniques

14:35 to 15:00

Cong Hongbo (DNV Columbus Inc., Dublin, USA), John R. Scully, Claes Taxen, R. Verley

Effects of Selected Water Chemistry Variables on Copper Pitting **Propagation: Experiments and Modeling**

15:00 to 15:25

Bo Rosborg (*The Royal Institute of Technology, Div. Surface and Corrosion Science,* Stockholm, Sweden), Jinshan Pan

The Corrosion Behavior of Pure Copper in a Bentonite/Saline Groundwater Environment

15:25 to 15:40

Coffee Break

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15:40 to 16:05

Thomas David Burleigh (Materials and Metallurgical Engineering Dept. New Mexico Tech, Socorro, USA), Drew Prichard

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Designing Color Stable, Tarnish Resistant, Copper Alloys

16:05 to 16:30

Kazuhisa Azumi (*Graduate School of Engineering, Hokkaido University, Sapporo, Japan*), Jungo Yajima

Evaluation of Copper Corrosion Rate in Underground Water at High Temperature Using Resistometry

16:30 to 16:55

Mengyan Nie (National Centre for Advanced Tribology at Southampton, Southampton, United Kingdom), Andy W. Cranny, Nick R. Harris, Mengyan Nie, Keith R. Stokes, Julian A. Wharton, Robert J. K. Wood

Crevice Solution Chemistries Evolution of Nickel-Aluminium Bronze in 3.5% NaCl Solution

Light Metals III, Al

Multi-purpose room

Chairs: J. Payer, P. Marcus

1	4:	1	0	to	1	4:35
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Georges Kipouros (*Materials Engineering, Dalhousie University, Halifax, Canada*), Paul Bishop, Michael Mosher, Hans Claus Neubing

Corrosion characteristics of Powder Metallurgy (P/M) aluminum alloys

14:35 to 15:00

Jinfeng Li (Department of Materials Science and Engineering, Columbus, USA), Gerald Frankel

Corrosion of an Al-Mg-Si alloy under MgCl₂ Solution Drops

15:00 to 15:25

Y. Yoon (University of Dayton Research Institute, Dayton, USA), M. Bouchard, K. Lafdi, L. Li

Corrosion Monitoring with CNT-Enhanced Fiber Sensors

15:25 to 15:40

Coffee Break

Wednesday, May 5, 2010 - Afternoon

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Wednesday, May 5, 2010 - Afternoon

8th Spring Meeting of the International Society of Electrochemistry

15:40 to 16:05

David Starosvetsky (Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel), Yair Ein-Eli, Tal Zaid

Passivity, Breakdown and Etching Rates of Silicon in Alkaline Solutions

16:05 to 16:30

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page 60

Brendy Rincon Troconis (Fontana Corrosion Center, The Ohio State University, Columbus, USA)

Effects of Surface Treatments on Adhesion Strength of Epoxy Coated AA2024-T3 Using the Blister Test

16:30 to 16:55

Yang Guo (Department of Materials Science and Engineering, Columbus, USA), Gerald Frankel

Corrosion Protection of Aluminum Alloys by Trivalent Chrome Process Treatment

Oil/Gas/Pipeline Corrosion II

Eastman Hall

Chairs: S. Nesic, B. Tribollet

14:10 to 14:35 Invited

Mark E. Orazem (Department of Chemical Engineering, University of Florida, Gainesville, USA), Douglas P. Riemer

Mathematical Models for Cathodic Protection of Pipelines

14:35 to 15:00

Bernard Tribollet (LISE UPR 15 du CNRS, Paris cedex 05, France), Didier Caron, Sylvain Fontaine, Ibrahim Ibrahim, Suzanne Joiret, Michel Meyer, Hisasi Takenouti

AC Corrosion Mechanism on Buried Pipelines

15:00 to 15:25

Luciano Lazzari (*Politecnico di Milano - Dipartimento di Chimica, Milan, Italy*), Andrea Brenna, Maria Vittoria Diamanti, Marco Ormellese Effects of AC on Passive Metals Corrosion

15:25 to 15:40

Coffee Break

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page 122 *Srael Institute*

15:40 to 16:05

Mariano Iannuzzi (Det Norske Veritas, Høvik, Norway), Luciano Avila-Gray, Gustavo Maio, Conchita Mendez

Electrochemical Noise Analysis to Determine Critical Pitting and Crevice Temperatures in Simulated Sour Environments

16:05 to 16:30

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page 69

Yoon-Seok Choi (Institute for Corrosion and Multiphase Technology, Department of Chemical and Biomolecular Engineering, Ohio University, Athens, USA), Shiun Ling, Srdjan Nesic

Effect of H₂S on the CO₂ Corrosion of Carbon Steel in Acidic Solutions

16:30 to 16:55

page 139

Yang Yang (Institute for Corrosion and Multiphase Technology, Department of Chemical and Biomolecular Engineering, Ohio University, Athens, USA), Srdjan Nesic, Bruce Brown

Development of an Electrochemical Quartz Crystal Microbalance Probe for Corrosion Testing in Flow Loops
Poster Presentations

Advances in the Science and Technology of Corrosion

Monday, May 3, 2010

17:00

First poster session in the late afternoon with a reception

Wednesday, May 5, 2010

Second poster session after lunch

s01-P-001

Nikolai Boshkov (Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria), Vasil Bachvarov, Desislava Koleva, Miglena Peshova, Petar Petrov, Georgi Raichevski, Neli Tsvetkova, Stefana Vitkova

Sustainability of Composite Zinc and Zinc-Based Deposits Additionally Treated in Environmentally Friendly Conversion Solution

s01-P-002

Andrea Brenna (Politecnico di Milano, Dipartimento di Chimica Materiali Ingegneria Chimica "G. Natta", Milan, Italy), Fabio Bolzoni, Marco Ormellese, MariaPia Pedeferri

Effect on Time-To-Corrosion of Chloride-Induced Corrosion of Reinforced Concrete Structures

s01-P-003

Severine Cambier (*Materials Science Engineering, The Ohio State University, Columbus, USA*)

Effects of Ozone and UV on Polymer Coating Degradation and Corrosion of Metal Substrates

s01-P-004

Liu Cao (Materials Science and Engineering, The Ohio State University, Columbus, USA), Gerald Frankel, Narasi Sridhar

Corrosion and Cracking of Carbon Steel in Fuel Grade Ethanol – Exploration of Supporting Electrolyte

s01-P-005

Ashwini Chandra (Fontana Corrosion Centre, Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), Gerald Frankel, Michael Sumption

Electropolishing of Niobium to Obtain Defect Free Surface

Xi Chen (Fontana Corrosion Center, The Ohio State University, Columbus, USA) Corrosion Resistance Assessment of Pre-Treated Magnesium Alloys

s01-P-007

Anusha Chilukuri (Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), Rudolph G Buchheit

Evaluation of the cathodic inhibition by rare earth (Ce^{3+} , Pr^{3+} , La^{3+}) and Zn^{2+} cations on AA 2024-T3 alloy and characterization of cation exchanged bentonite pigments dispersed in organic coatings

s01-P-008

Jose M. Costa (Department of Physical Chemistry, University of Barcelona, Barcelona, Spain)

The Records of Atmospheric Corrosion Study: Facts and Figures

s01-P-009

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Silviu Iulian Drob (Electrochemistry and Corrosion, Institute of Physical Chemistry, Bucharest, Romania), Paula Drob, Mihaela Mandroiu, Cristian Pirvu, Ecaterina Vasilescu, Cora Vasilescu

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Hidenori Fujii (Higashimaru Shoyu Co., Ltd, Tatsuno, Japan)

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Belinda L. Hurley (Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), Rudolph G. Buchheit

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Mariano Kappes (Fontana Corrosion Center, The Ohio State University, Columbus, USA), Ricardo Carranza, Gerald Frankel, Narasi Sridhar, Ramgopal Thodla

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Borna Kazerooni (Center for Electrochemical Science and Engineering, Department of Materials Science and Engineering, University of Virginia, Charlottesville, USA), Wasiu Adedeji, Robert Kelly

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s01-P-016

Halina Krawiec (AGH University of Science and Technology, Department of Chemistry and Corrosion of Metals, Krakow, Poland), Jacek Banas, Alicja Lukaszczyk

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Hyuk Sang Kwon (Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, DaeJeon, Korea), Se Jin Ahn, Kyung Jin Park

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Nushe Lajci (University of Prishtina, Faculty of Mines and Metallurgy, Republic of Kosova, Mitrovica, Albania), Mirjana Metikos-Hukovic, Zeljka Petrovic Chromium Passivity in Sulfuric Acid Solution

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Xiaoji Li (Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), Sean Brossia, Hongbo Cong, Gerald S. Frankel, Feng Gui, Belinda L. Hurley, Xiaoji Li

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Huang Lin (Fontana Corrosion Center, The Ohio State University, Columbus, USA), Gerald Frankel

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Changjian Lin (State Key Lab of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, China), Shigang Dong, Ronggang Hu, Lanqiang Li

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Digby Macdonald (Materials Science and Engineering, Pennsylvania State University, University Park, USA), Jan Mankowski

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Bastian Maier (*The Ohio State University, Columbus, USA*), G.S. Frankel Investigation of defects in Mg-rich primer on AA2024-T3

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M. F. Mohamed (Institute for Corrosion and Multiphase Flow, Ohio University, Athens, USA), Srdjan Nesic, A. Muhammad Nor, M. Singer, M.F. Suhor Corrosion prediction model enhancement for high pressure CO₂ environments

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A. Mohammed Nor (Institute for Corrosion and Multiphase Technology, Ohio University, Athens, USA), M. F. Mohamed, S. Nesic, M. F. Suhor Mass Transfer Characterization of Thin Channel Flow Cell for Flow-Sensitive CO₂ Corrosion Study

Rajendran Nallayan (Department of Chemistry, Anna University Chennai, Chennai, India), Karthega Mani

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s01-P-029

Thoa T. P. Nguyen (University of Science, Vietnam National University, Ho Chi Minh City, Viet Nam), Hai V. Le, Tru N. Nguyen

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s01-P-030

Chike Oduoza (University of Wolverhampton, SEBE, Wolverhampton, United Kingdom)

White Bronze Plating as a Possible Substitute for Nickel in Decorative Chromium Plating

s01-P-031

Soo-Gil Park (*Chungbuk National University, Cheong-ju, Korea*), Hong-Il Kim, Han-Joo Kim, Dal-Woo Shin, Jeong-Jin Yang

Effect of additive on etching pit behavior of aluminum under AC etching process

s01-P-032

Ralf Posner (Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University, Columbus, USA), Galina Giza, Guido Grundmeier

Investigation of the polymer/oxide/metal interface stability with an *in-situ* Scanning Kelvin Probe Blister Test

s01-P-033

Masatoshi Sakairi (Graduate School of Engineering, Hokkaido University, Sapporo, Japan), Tatsuya Kikuchi, Youichi Kojima, Yoshiyuki Oya, Kenji Yanada

Formation and corrosion behavior of artificial pit of 2024 aluminum alloy with PRM

s01-P-034

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Electrochemical behaviors of AZ31 and AZ91 Mg alloys in alkaline and chloride solutions

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Effect of Operation Conditions During Plating on Electrochemical Behavior and Morphology of Chromium Films

s01-P-036

Joao Tedim (Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal), Mario Ferreira, Silvar Kallip, Alena Kuznetsova, Andrei Salak, Mikhail Zheludkevich

Application of Nanostructured Materials as Host Structures for Corrosion Inhibitors

s01-P-037

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In-situ Monitoring Undercoating Corrosion Damage of Al Thin Film by Direct Optical Interrogation (DOI)

s01-P-038

Aide Torres-Huerta (CICATA-Altamira, Instituto Politécnico Nacional, Altamira, Mexico), Silvia Brachetti-Sibaja, Miguel Domínguez-Crespo, Esther Ramírez-Meneses, Aide Torres-Huerta

Electrochemical characterization of Ce (La)-based coatings on commercial AA6061 aluminum alloy

s01-P-039

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Effect of Metal Glass Coating on the Electrochemical and Corrosion Behavior of 316L Stainless Steel Bipolar Plate for Fuel Cell Application

s01-P-040

Ecaterina Vasilescu (Electrochemistry and Corrosion, Institute of Physical Chemistry, Bucharest, Romania), Jose Maria Calderon Moreno, Paula Drob, Silviu Iulian Drob, Cora Vasilescu

Monitoring of Some New Scaffolds Behavior in Simulated Body Fluid

s01-P-041

Cora Vasilescu (Electrochemistry and Corrosion, Institute of Physical Chemistry, Bucharest, Romania), Paula Drob, Silviu Iulian Drob, Monica Popa, Ecaterina Vasilescu

Passivity Behavior and Long Term Stability of a New Non-toxic Implant Alloy

Jesús Manuel Vega Vega (Department of Material's Engineering, Degradation and Durability National Centre for Metallurgical Research (CENIM/CSIC), Madrid, Spain), Belén Chico, Daniel de la Fuente, Iván Díaz, Noelia Granizo, Manuel Morcillo, Joaquin Simancas

Inhibition Mechanism and Anticorrosive Behaviour of Calcium Exchanged Silica Pigment

s01-P-043

Liang Zhenhai (College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, China), Caimei Fan, Xiaogang Hao

Corrosive Performance of Ti/SnO₂+Sb₂O₄/CF/PbO₂Acid-Proof Anode

s01-P-044

John Zimmerman (Henkel, Madison Heights, USA), John Comoford, Ronald Dubs, Girdhari Kumar, Kirsten Lill

Comparison of Semiconductor Properties for Pretreatments on Steel: Progress Toward Characterization and Performance Prediction for Zirconium Nanoscale Coatings (Zr-nsC)

Keynote Lectures



Multi-Scale Modeling of atmospheric Corrosion.

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A multi-scale model of the atmospheric corrosion of metals is being developed and can be classified into two parts. Part 1 is based on integrating modules that define such processes as marine aerosol production by oceans and breaking surf, transport of marine aerosols across landscapes, deposition of aerosols onto structures, cleaning of surfaces by wind and rain, and the wetting and drying of surfaces throughout surface temperature and relative humidity cycles. The integration of these modules into a software framework enables the user to extract accurate estimates of surface conditions for structures located at any geographical location in Australia. Part 2 is aimed at developing a more fundamental approach to estimating corrosion based on the response of a metal to its environment .At present the focus is on understanding the corrosion processes that occur under a droplet and developing a model of a porous oxide.

The droplets that form on a metal cover the surface with a moisture layer of varying thickness and thus variations in dissolved oxygen may induce a spatial separation of the anodic and cathodic reactions on a length scale characteristic of the roughness and the local energetics of the system. This leads to a spatial and temporal variation of species concentrations, current and potential over the metal surface and thus atmospheric corrosion. Here a two dimensional model is developed addressing the corrosion of a metal under an aerosol droplet. The effect of various parameters like exchange current densities, initial concentrations, shape and size of the droplet and diffusivity of oxygen on the evolution of the anode-cathode separation are investigated. The oxide that develops on the surface of the metals like zinc is usually porous. Any further oxidation of the metal can happen only if the electrolyte percolates through the oxide and comes in contact with the metal and also only if there is a provision for the cathodic reaction to happen elsewhere. In most systems like zinc, this cathodic reaction is usually oxygen reduction reaction. This reaction, depending on the conditions could take place either on the metal surface or on the porous oxide surface. That is, the porous oxide matrix could also conduct electrons which, at contact with the electrolyte in the pores, may lead to oxygen reduction locally. However the anodic reaction namely the metal dissolution would occur only on the metal surface since free metal is not available for corrosion anywhere else. The present one-dimensional model investigates the role of various parameters like work function of the metal and metal oxide, metal oxide conductivity, exchange current densities of anodic and cathodic reactions, porosity and tortuosity on the extent and location of the cathodic reaction. Also conditions leading to passivation are identified.

An overall framework is being develop to integrate Part 1 of the model development with the components of Part 2. Relevance of the model to global variations in atmospheric corrosion and the design of metals and oxides to reduce corrosion is discussed

The Early History of Passivity Research at the Fontana Corrosion Center

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The Point Defect Model, which arguably provides the best description of passivity yet devised, had its genesis in the Fontana Corrosion Center in the early 1980s. While the original model had to be modified to recognize dissolution of the defective barrier layer and to recognize the formation of a precipitated outer layer, in order to avoid the objections to the High Field Model (HFM, and variants, thereof), the later versions have been remarkably successful in describing the growth and breakdown of passive films under a wide range of environmental conditions. In this presentation, we will trace the development of the PDM from the initial inception in the FCC in 1979 to its current form, with particular emphasis on its ability to account for wide-band-width electrochemical impedance spectroscopy (EIS) data, the steady-state polarization data, the electronic character of passive films in terms of the dominant defect, and its ability to account for alloying, photo inhibition, and the effects of chloride ion activity and pH on the passivity breakdown voltage and induction time. Finally, the potential sweeprate dependence of the critical breakdown voltage provides an unequivocal test of the PDM, by yielding the concentration of condensed cation vacancies at the metal/barrier layer interface, which are found to be in good agreement with values calculated from structural arguments.

Passivity and Passivity Breakdown: a Combined Experimental and Atomistic Modeling Approach.

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Recent advances in the understanding of passivity and passivity breakdown, combining experiments and models at the nanoscale, will be presented. Three aspects will be emphasized :

1 – Investigation of corrosion/passivation of metals (Cu, Ag, Ni) and alloys (ferritic and austenitic stainless steels) using high resolution local probes (EC-STM, EC-AFM) including adsorption of hydroxyls, growth and stability of oxide layers, and initiation of localized corrosion (pitting).

2 – New development in methods for the characterization of passive films : the use of tunnelling spectroscopy to investigate the local electronic structure of passive films.

3 - Atomistic modeling of corrosion processes using DFT, with emphasis on the interplay between aggressive environmental species (CI⁻) and structural factors of the material surface (defects).

The "Wedging Action" of Compounds as a Damage Process Important to Professor Fontana

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"Font" was always interested in expanding corrosion products as important in various damage processes. Such damage occurs in the expansion of corrosion products on reinforcing bars in concrete and welded joints. He also felt that such damage was important to the initiation and propagation of stress corrosion cracking. This expansion of compounds, oxides, was first calculated and summarized for various metals by Pilling and Bedworth (J. Inst. Met. 29, 534, 1923) in 1923. However, the forces exerted by growing crystals was first identified in a reference by Becker and Day (Proc. Wash Acad Sciences, VII, 283, 1905) in 1905 who referred also to studies by Jean Lavalle in 1853 and by Lehmann in 1888 on the same subject. Forces exerted in concrete by the expansion of corrosion products from corroding reinforcing bars were studied and forces measured in detail by Rosa et al. (#18 Bu. Standards 1919 GPO) and reported in 1919. Similar work was undertaken in his MS thesis and reported by Rosengarth (MS, 1981 Penn State Univ) in 1981. In 1962 Pickering et al. (Corr. Jnl. 18, 1962) showed that the force of corrosion products grown in a crevice could be measured for specimens of stainless steel exposed to 200°C chloride electrolytes. In this same paper, they showed that the forces in a crevice would produce sufficient stresses at the bottom of a crevice to initiate SCC; thereupon they removed the crevice element and the SCC continued to grow due only to the forces of expanding corrosion products inside the SCC. This is illustrated in Figure 1. Of substantial economic concern has been the growth of corrosion products inside the superheated crevices of tube supports in the steam generators of pressurized water reactors as summarized by Staehle. Such expansion causes the tubes to deform and sustain SCC at locations of high plastic strains as shown in Figure 2. Other recent results associated with the presence of lead impurities in these superheated crevices have shown that the lead greatly accelerates oxidation of Alloy 690 tubing (Proc. 5th CNS SG meet). Professor Fontana's instincts again demonstrated that his intuitions in corrosion were right.



Novel Approaches to an Old Problem: Selective Dissolution of Binary Alloys

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Each year corrosion causes huge losses for the society. Yet, most of the relevant processes are not even understood in their basics. As most chemistry, corrosion is taking place on the atomic or molecular scale and recent progress in experimental techniques have enabled a new view on relevant processes. Selective dissolution of alloys composed of elements with largely different equilibrium potentials is a good example. Here I present recent progress in understanding the model system Cu-Au obtained by in-situ scanning probe techniques, in-situ diffraction employing synchrotron radiation, and scanning Auger electron spectroscopy.

Oral Presentations



Hexafluorozirconic Acid Based Surface Pretreatments as a Replacement for Phosphate Conversion Coating: Characterization and Performance Assessment

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Phosphate conversion coatings have historically the most commonly used surface pretreatments for ferrous and non-ferrous metals. However, with the growing concerns over the environmental impact of phosphates, new environment-friendly surface treatments need to be developed, without compromising on the corrosion protective performance of the phosphate coatings.

A new phosphate-free pretreatment from Henkel Surface Technologies called Bonderite® TecTalisTM, made by modifying a dilute hexafluorozirconic acid (H_2ZrF_6) by adding small quantities of non-hazardous components was investigated and characterized in this study and compared to performance of phosphate conversion coatings and simple hexafluorozirconic acid. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) were used to characterize the coating surface morphology, structure and composition. Quartz Crystal Microbalance (QCM) was used for studying film growth kinetics on thin films of pure Fe, Al and Zn. Electrochemical Impedance Spectroscopy (EIS) was performed on painted steel for studying long-term corrosion performance of the coatings.

EIS results for painted cold rolled steel (CRS) substrates showed that TecTalis provides good long term corrosion protection on application of paint, comparable to that of phosphate conversion coatings. QCM results showed that for all thin film substrates of Fe, Al and Zn, the coating growth rate is higher for TecTalis as compared to the hexafluorozirconic acid only bath. AFM of TecTalis treated CRS surfaces showed that the surface is uniformly covered with small nodules ~20 nm in size and clusters of these features that were 100-500 nm in diameter. Clusters exhibited 20-30 mV higher surface potentials than other parts of the coating indicating lesser activity. TEM results indicated that the TecTalis coating is about 30 nm at most locations. The TecTalis coatings are mostly composed of Zr and O with Fe and F enriched closer to the coating-CRS interface.

Keywords: surface pretreatment, phosphate conversion coating, cold rolled steel, corrosion protection, hexafluorozirconic acid.

Acknowledgement: This work has been sponsored by Henkel Surface Technologies (Madison heights, MI, USA).

Evaluation of Hydrogen Embrittlement Property of High Strength Steels

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The demand for high strength steels with higher strength is increasing for lightning of construction components, automobile parts and so on. Newly developed 1400 MPaclass steel has been already used practically for fasteners [1]. However, as it is well known, high strength steels are susceptible to hydrogen embrittlement (HE) [2, 3], and evaluation HE property becomes more important issue for safe usage and development of advanced high strength steels. Since diffusible hydrogen is considered to cause HE [4], critical hydrogen content for HE fracture is used as a parameter for evaluation of susceptibility of high strength steels to HE [5]. Hydrogen entry from the service environment should be also taken into account for the evaluation of HE property [5].

In this study, slow strain rate tests (SSRT) of circumferentially notched round bar specimens of AISI 4135 steel with 1500 and 1300 MPa of tensile strength (TS) and boron baring steel with 1300 MPa of TS have been carried out after cyclic corrosion test (CCT) or outdoor exposure. During SSRT the atmosphere around the specimen was kept wet to reproduce active corrosion influenced by the rust layer and to keep corresponding hydrogen entry. After SSRT, hydrogen content in the fractured specimen was measured by means of thermal desorption spectrometry.

The fracture stress of the AISI4135 steel with 1500 MPa of TS showed obvious decrease in fracture stress with increase of hydrogen content and its fracture surface indicated clear intergranular fracture. The AISI 3135 steel with 1300 MPa of TS decreased less significantly in fracture stress than the steel with 1500 MPa of TS. The boron baring steel showed no clear decrease in fracture stress suggesting its higher resistance to HE. Thus, HE property was successfully evaluated by the method in consideration of hydrogen entry and its influence on mechanical property. In order to ascertain if the wet condition applied during SSRT is suitable to reproduce active hydrogen entry, electrochemical hydrogen permeation test of pure Fe sheet after CCT was carried out to investigate the influence of wetness of the atmosphere on hydrogen entry. Furthermore, influence of humidity on corrosion rate measured by means of atmospheric corrosion monitoring censor [6], which experienced the same CCT process, was also conducted to investigate influencing factors for hydrogen entry.

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Alkoxysilane Oligomer Modified Epoxide Primers for Automotive Coatings

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Telechelic resins with reactive end groups (epoxy phosphate and epoxy ester) were synthesized using bisphenol-A (BPA) epoxide. The bisphenol-A based epoxide, the epoxy phosphate, and the epoxy ester were all modified with tetraethylorthosilicate (TEOS) oligomers, which were prepared through the hydrolysis and condensation of TEOS monomer with water under acidic condition. The epoxide/polysilicate (organic/inorganic) hybrid systems were characterized systematically, using FTIR; ¹H, ¹³C, ³¹P, and ²⁹Si NMR, and MALDI-TOF. The modified epoxides were thermally cured with a melamine-formaldehyde resin, cast on steel substrates. The coating performance of the modified epoxides were evaluated by pencil hardness, crosshatch adhesion, reverse and direct impact resistance, mandrel bending, and pull-off adhesion. Viscoelastic properties of the hybrid systems were also evaluated as a function of polysilicate content. Corrosion performance was evaluated via salt spray (fog) test for 264 hours. Salt spray analysis revealed that inorganically modified epoxides provided improvement over the unmodified epoxide resins with respect to both corrosion resistance and adhesion to steel substrates.

Keywords: Sol-gel; Epoxides; Phosphates; Fatty Acids; corrosion; Salt Spray; Coating Properties; Dynamic Mechanical Properties

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Study of chromium-free passivation process of Ti-P-Si-Mo compound system for electrogalvanized coating

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The application of traditional hexavalent chromium passivation has been gradually restricted for its toxicity and harm to environment. Therefore the development of a substitute process without pollution of chromate becomes a top priority. The comparison research was carried out on the passivation result of Ti-P-Si-Mn compound system, Ti-Zr-Si compound system and Ti-P-Si-Mo compound system. The result shows that the passivation result of Ti-P-Si-Mo compound system is better than that of other systems, and more comparable to that of chromate.

The compositions and process conditions of Ti-P-Si-Mo compound system are $1.8ml\cdot L^{-1}$ H₃PO₄, $2.8ml\cdot L^{-1}$ HNO₃, $18g\cdot L^{-1}$ Na₂SiO₃·9H₂O, $10.0ml\cdot L^{-1}$ TiCl₃, $0.85g\cdot L^{-1}$ Na₂MoO₄·2H₂O, passivation temperature of room temperature, passivation time of 25s,

drying temperature of 65 $^{\circ}$ C and drying time of 15min. A blue and white nonchromium passivation film is obtained by use of this processing, and the corrosion resistance of the film can endure 48h in neutral salt spray experiment.

The surface morphologies of passivation films passivated from Ti-P-Si-Mo compound system were observed by scanning electron microscopy (SEM). The results show that the crystallization of the passivation films from Ti-P-Si-Mo passivation is finer than that from trivalent chromate passivation. The chemical state of the passivation films were analyzed by X-ray photoelectron spectroscopy (XPS). The results show that the passivation films are composed of TiO_2 , ZnO, $Zn_3(PO_4)_2$, $Zn(H_2PO_4)_2$, $Zn_2SiO_4/ZnSiO_3$, $Zn_4Si_2O_7(OH)_2 \cdot 2H_2O$, MoO_3/MoO_4^{2-} , MoO_2 and MoO(OH). The contact angle testing shows that the surface hydrophobic properties of the passivation films are superior to that from Cr^{3+} passivation system. Based on the analysis above, the film formation mechanism of Ti-P-Si-Mo passivation films is put forward. The passivation films are composed of the compound deposition of titanium, phosphorus, silicon, molybdenum compounds. The excellent corrosion resistance of the passivation film is because of the co-operation action of deposition corrosion inhibition of titanium and silicon compounds and anodic passivation corrosion inhibition of molybdate.

Key words: non-chromium passivation, Ti-P-Si-Mo compound passivation, galvanized coating, corrosion resistance

Non-Contacting Method For The Corrosion Rate Measurement In Concrete Structures: Study About The Correct Electrical Model To Be Applied

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In order to measure metal corrosion it is necessary to make physical contact with the metallic piece which acts as working electrode. The most widely used method for determination of corrosion current is an electrochemical method, the so called, Polarization Resistance method. In a previous paper, the feasibility of using a new method for polarizing the metal without the need of physical contact with it, was presented (1). The polarization is obtained through the induction of a current by means of an external electrical field. In that paper, the model proposed for the calculation of the corrosion rate assumed that the current runs in parallel through the electrolyte and the metal, and the current electrostatically polarizes the metal. In the present paper, a wide study about the model use and the different possibilities that appears when the electrolyte resistance is represented in two different components is discussed.

In order to study which current distribution is the most feasible, tests with several analogue circuits were made. Three electrical circuits were prepared to study their responses to the application of a current step. The circuits studied are shown in Figure 1.



Figure 1. Circuits studied: C1, C2 and C3.

In these circuits, Re' represents the part of the path going from the injection point (electrode) to the metal (working electrode), and Re'' the path along the working electrode. R_M is the metal resistance.

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Perspective on SCC Response and Prediction in Nuclear Power System

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Reliable operation of commercial nuclear power depends on good resistance to stress corrosion cracking of structural material in high temperature water. Plant life extension well beyond the original design life is being aggressively pursued, as is the construction of hundreds of new plants whose life expectancy is targeted at 60 - 80+ years. Dozens of material – environment systems have proven inadequate to these requirements, and demonstrating adequate resistance requires sophisticated experimental and modeling / prediction capabilities. A confluence of metallurgy, chemistry, electrochemistry, mechanics, radiation, and other disciplines is involved in environmentally assisted cracking.

All structural materials – from ferritic steels to austenitic stainless steels to nickel allolys – share many SCC dependencies in common, and it seems likely that the underlying processes and mechanisms are also shared. The same applies to the spectrum of environments, especially from boiling water reactor (BWR) normal water chemistry, to BWR hydrogen water chemistry to pressurized water reactor (PWR) primary water. The common underlying response points to a common basis for predicting the growth rate of cracks across the spectrum of materials and environments, and provide a basis for optimism that reliability and long life can be achieved.

Integrated Sensor Networks for Corrosion Under Insulation: Monitoring, Cost Reduction, and Life Extension Strategies Part 1: Monitoring - Detection Of Cui

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System health assessment using sensor networks has been used in the past to detect the presence of Corrosion Under Insulation (CUI) and coating. Corrosion sensors placed under insulation offer a replacement or alternative to expensive inspections. If installed during the early project design stage, sensor networks can greatly reduce the need for inspection and unexpected replacement costs.

This paper shows three different techniques to detect the presence of moisture and its corrosiveness. The techniques are: direct impedance measurement, the combination of galvanic couple with active RFID tags and Wi-Fi based motes connected to 2 wires electrodes. While all techniques were able to detect CUI, only one can be used to create an intelligent wireless sensor network capable to detect CUI. This paper also demonstrates the efficiency of smart sensor networks to detect CUI and propose the architecture for an intelligent sensor network designed to detect the presence of CUI in an early stage. The following parts will demonstrate how to create an intelligent sensor network, and how to model corrosion risk using the large amount of data generated by a sensor network.

Keywords: remote monitoring, system health assessment, integrity, corrosion sensors, CUI, mote, Wi-Fi.

Evaluation of Copper Corrosion Rate in Underground Water at High Temperature using Resistometry

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Copper is one of candidate of container metal for high level radioactive nuclear waste in glassificated form. Advantage of copper for this purpose is that it does not corrode in environment without oxygen, and such condition will be established after long period burying due to consumption of oxygen around the container. Corrosion behavior of copper in the condition before complete depletion of oxygen in the underground water has therefore to be investigated. For this purpose we used resistometry method in which electric resistance change of very thin copper foil immersed in high temperature electrolyte solution containing ions existing in underground water was measured and reduction of cross sectional area of foil, i.e., loss of metallic copper was calculated from increase in resistance value. To reduce the influence of temperature fluctuation on resistance of metal specimen, two copper foil was embedded in laminate sheet. One of two foils was exposed to the electrolyte solution and another was protected from corrosion by complete sealing with the laminate sheet. Resistance change of corroding foil was thus measured as a relative value to the sealed foil. Corrosion rate was evaluated as a function of temperature, dissolved oxygen (DO) concentration and kind of ionic species. For example, at 80°C, copper corroded continuously in 0.01 M Na₂SO₄ solution while corrosion rate was considerably reduced in 0.01 M NaHCO₃ solution. When Copper was immersed in 0.01 M NaHCO₃ solution more than 100 ks and then Na₂SO₃ was added, corrosion did not become obvious. Addition of 0.01 M NH₃Cl to water considerably accelerated corrosion as shown in Fig.1. On the other hand, effect of air injection, i.e., increase in DO, on corrosion rate was not clear.



Fig.1 Changes in relative resistance expressed as AC signal of corroding Cu foil immersed in water, DO and temperature of solution. NH₃Cl was added at ca. 250 ks.

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Use of electrochemical atomic force microscopy to understand the localised corrosion of light metals

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Corrosion of most engineering alloys is a very localized phenomenon, with initiation and propagation often dictated by nanoscale microstructural heterogeneities that can have markedly different electrochemical properties than the matrix. Measurement and resolution of electrochemical phenomena on the nanoscale is critical to understanding the microstructure-corrosion relationship and subsequently controlling it.

This work presents results from an AFM based in-situ corrosion probing methodology capable of resolving the electrochemical activity into the nanometer range. With the ability to image alloy microstructural features of interest via AFM and within an electrolyte - one can probe electrochemical phenomena in the mircostructural vicinity of interest. This technique is deployed in order to address some of the origins of localized corrosion in both aluminium and magnesium alloys.

Oral Presentations

Characterizing the Relationship between EIS Measurements and Exposure Testing Results Using Neural Networks and Fuzzy Set Theory

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Electrochemical impedance spectroscopy measurements and cabinet exposure testing methods are both used to evaluate the protectiveness of corrosion resistant organic coatings on metals. In this study, fully connected three-layer feed-forward artificial neural network (ANN) models were developed to relate the results of EIS measurements from samples exposed to ASTM B117 salt spray exposure experiments made after short sample exposure times (48 hours) to the extent of coating and sample corrosion damage after 30 days of exposure. To train the models, nearly 1000 individual measurements were collected from 30 different coating systems applied to aluminum alloy 7075-T6 substrates. Using this large data set, several ANN models were developed relating EIS data (e.g., impedance modulus, phase angle) directly time to failure (TTF) in exposure testing. The output of the models was relationships that enabled prediction of TTF in exposure testing from measured impedance spectra. The best models enabled remarkably accurate estimates of TTF from EIS spectra measured in the first two days of exposure. A sensitivity analysis of ANN model output based on fuzzy set theory showed that variations in the impedance spectra in the frequency range of 100 to 2000 Hz and near 0.01 Hz were most important in making an accurate forecast of coating life. The higher frequency range typically corresponds to the range where the upper breakpoint frequency is observed for organic coatings that are beginning to fail. The lower frequency range is indicative of overall corrosion damage accumulation on the sample. These findings corroborate much work reported in the literature on interpretation of EIS response from organically coated metals by showing that the EIS response in intermediate and low frequency range windows contains information that is important to making an accurate forecast of coating protectiveness in long-term exposure measurements. These findings also extend current understanding by showing that models that predict long-term exposure results from short-term EIS measurements are possible.

Keywords: Coatings, electrochemical impedance spectroscopy, exposure testing, artificial neural networks, fuzzy set theory.

Designing Color Stable, Tarnish Resistant, Copper Alloys.

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In order to design color stable, tarnish resistant, copper alloys, we need to understand why some copper alloys have better tarnish resistance than other alloys. Tests have been conducted to correlate the corrosion resistance of nine commercial copper alloys to their composition and to the properties of their surface oxides. A tarnish chamber was used to measure the atmospheric tarnish resistance of the alloys. Electrochemical tests, including potentiodynamic polarizations, electrochemical impedance spectroscopy (EIS), and Mott-Schottky were used to determine the corrosion rate, thickness, and the semiconductor properties of the surface oxide films, while immersed in a sulfide electrolyte.

We found that by using a solution of 1mM Na₂S + 2mM NaOH, we were able to correlate the atmospheric tarnish resistance with the electrochemical corrosion results. Alloys with a zinc content >17% Zn had an increased corrosion potential and lower passive current densities. The oxide films on these same alloys were also shown to have higher impedance, or thickness than other alloys, as shown in Figure 1. Tarnish chamber testing showed that these same alloys

with the high zinc content were also among the most tarnish resistant samples.



Figure 1: Comparison of nine commercial alloys in a slightly basic, sulfide solution.

Based upon our current research results, several new copper alloys are being cast and tested as we attempt to develop a color-stable, tarnish resistant, copper alloy. A sweat test baton is also being constructed out of multiple copper samples for testing the different alloys' resistance to hand contact.

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Effect of intermetallic content on the pit stability and propagation kinetics of duplex stainless steel exposed to CO₂ saturated production brine

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Pit stability and growth kinetics were evaluated for 2205 (UNS S32205) and 2507 (UNS S32750) duplex stainless steel (SS) samples that had been heat treated in order to produce volumetric fractions of intermetallic compounds between 0-14% dispersed within the ferrite grain boundaries. The study was performed in conditions simulating oilfield production brine, using saturation at 1 bar CO_2 , at 25^oC and 80^oC and the intermetallic content as the main independent variables.

Experimental evaluation of pit growth was done using galvanostatic polarization between 10μ A/cm² up to 1mA/cm², coupled with potentiodynamic polarization scans to evaluate the repassivation behavior. Complimentary cyclic polarization was used to assess the behavior of the critical parameters associated with pit nucleation and stability.

The results indicate that the minimum current for stable diffusion controlled pitting increases with temperature. However, it is found to decrease with intermetallic content in the duplex SS. Comparison of the results for both SSs indicates that pit stability is found at lower current densities for the 2205 duplex SS.

Estimation of pitting potentials from the values of the stable diffusion controlled pitting currents shows a difference with values observed from the polarization curves in both duplex SSs; this gap being consistent with the intermetallic phase content. These results suggest that at electrode potentials below those associated with stable pitting, localized dissolution occurs between the ferrite and the intermetallic phase's, leading to crevice corrosion behavior, which was found in the SEM inspection of the electrode surfaces (Figure 1).



Figure 1 .- SEM image of 2507 SS coupon with 2% intermetallic fraction, following testing galvanostatic testing at 20 μ A/cm² for 1200 s, in synthetic production brine saturated with CO₂ at 25°C.

Neural Network Modeling of Pit Growth Kinetics in Aluminum Alloys

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Components of aging aircraft utilize highstrength aluminum alloys that contain a large population of intermetallic particles, which renders them susceptible to localized corrosion [1]. Since these alloys are subject to cyclic loading and corrosion pits are capable of nucleating fatigue cracks [2], it is necessary to fully characterize pit growth Furthermore, aircraft with time. can experience various environments (including locally) throughout its lifetime, and therefore the environmental dependence of pit growth should be explored.

In this work, AA7075-T651 blocks were boldly exposed in environments of various temperature (0, 25, 40, 60°C), pH (2.5, 6, 10, 12.5), and [Cl⁻] (0.01, 0.1, 0.6M NaCl) and removed after 1, 24, and 720 hours. Additionally, two metallurgical faces (LS, ST) that represent the orientations exposed in rivet holes were studied. Optical profilometry was employed to measure a population of pit depths at each condition. Pit depth distributions were fit to a twoparameter Weibull.

Maximum pit depth and both Weibull parameters (α and β) were modeled using artificial neural networks. As shown in



Figure 1 Neural network predicted versus observed pit depth.



Figure 2 Comparison of observed (open symbols) and neural network-predicted (closed symbols) pit depth distributions.

Figures 1 and 2, the neural networks were able to accurately predict the maximum pit depth and the pit depth distributions as a function of environment.

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Effect of H₂S on the CO₂ Corrosion of Carbon Steel in Acidic Solutions

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The objective of this study is to evaluate the effect of low level hydrogen sulfide (H_2S) on carbon dioxide (CO₂) corrosion of carbon steel in acidic solutions, and to investigate the mechanism of iron sulfide scale formation in CO₂/H₂S environments. Corrosion tests were conducted using 1018 carbon steel in 1 wt.% NaCl solution (25°C) at pH of 3 and 4, and under atmospheric pressure. The test solution was saturated with flowing gases that change with increasing time from CO_2 (stage 1) to $CO_2/100$ ppm H₂S (stage 2) and back to CO_2 (stage 3). Corrosion rates were measured using linear polarization resistance (LPR) technique. Electrochemical impedance spectroscopy (EIS) and potentiodynamic tests were performed at the end of each stage. The morphology and compositions of surface corrosion products were analyzed using scanning electron microscopy (SEM) / energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The results showed that the addition of 100 ppm H_2S to CO_2 induced rapid reduction in the corrosion rate at both pH 3 and 4. This H₂S inhibition effect is attributed to the formation of thin FeS film (tarnish) on the steel surface that, suppressed the anodic dissolution reaction. It is postulated that the surface pH is different from bulk pH due to local supersaturation, and enabled the formation of stable FeS film on steel surface via precipitation.

Modeling of micro-galvanic corrosion

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In this work, we investigate the effect of microstructure, particularly the effect of β phase fraction and its distribution, on corrosion behavior of a metal alloy. Binary phase magnesium (Mg) alloy comprised of electrochemically active α phase and relatively nobler β phase is considered here, but the method can be extended to any binary phase alloy. A numerical model has been developed using a moving mesh technique in COMSOL Multi-Physics[®], which is capable of tracking the moving boundary of the corroding phase (α phase). The model predictions are based upon the electrode kinetics at the anode surface and the cathode surface, which are obtained by performing lab scale polarization experiments. The model is capable of incorporating non-linear polarization behavior of the α phase and the β phase using a piecewise linear approximation, where the current density data is available for every 1 mV change in the electric potential. The corrosion behavior of the metal alloy is dependent on the β phase fraction and its distribution, as well as aluminum (Al) content in the α phase. Here, we address the effect of β phase fraction and its distribution on corrosion behavior assuming uniform Al content in the α phase. A novel formulation using the level set function is used here in order to incorporate various microstructure configurations along the depth of the alloy. We consider various α phase - β phase configurations such as a continuous β phase network around the α phase, a discontinuous but well supported β phase network around the α phase, and a discrete β phase. The metal alloy with a continuous β phase network is found to have accelerated corrosion in the initial phase due to increasing β phase fraction. However, corrosion tends to be halted after the α phase is preferentially dissolved and the continuous β phase network is exposed to electrolyte due to β phase enrichment [1]. The numerical model can also predict a scenario leading to undermining of β phase from the surface, as reported in the literature [2] in case of the discrete β phase configuration. Thus, the role of β phase distribution on the corrosion behavior has been brought out in this work, thereby providing a better insight into understanding the effect of microstructure on corrosion.

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SVET-Study of the Electrochemical Behavior of Different Hot-Dip Zn-Based Coatings on Steel

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The corrosion of different industrial hot-dip galvanized steels was comparatively studied using voltammetry and Scanning Vibrating Electrode Technique (SVET). For this, interstitial free steel was hot-tip galvanized in pure Zn (HDG Zn), in Zn-43%Al-1%Si (HDG ZnAlSi) and in Zn-0.2%Al, followed by annealing (HDGA Zn0.2Al or *Galvanneal*). While HDG Zn shows an 3 μ m outer layer of Zn-rich η -phase (0.2%Fe) and an inner 2µm layer of ξ-phase, HDG ZnAlSi shows a 20µm dendritic structure of almost pure Al layer with no significant amounts of intermetallic phases and heat treated (galvannealled) HDG ZnAlSi has a 10 μ m columnar layer of δ -phase (FeZn₁₀) and a nanometric layer of γ (FeZn₄) on the Fe surface. Hydrogen reduction is similarly inhibited on all three coatings, but the anodic behavior in 0.1M NaCl is guite different. At high $\partial E/\partial t$ (50 my/s) the galvannealled coating HDGA dissolves anodically at more negative potentials (Fig.1a), while at a low $\partial E/\partial t$ (1 mv/s), the Al reach coating HDG Zn-43Al-1Si is more readily attacked already at -1V (Ag/AgCl) as shown in Fig 1b. A reverse peak is shown by HDG Zn and, more intensively, by HDGA Zn0.2Al. This is associated to a strong Fe-substrate corrosion, indicating that on the Al poor coatings the substrate is more easily exposed and attacked by localized corrosion. When large areas of the steel substrate are exposed to 0.1M Cl⁻, as in the case of a cross section of the coated steel, the behavior is also different. While cathodic areas are uniformly distributed on the steel surface, the protection produced by Zn depends on its localized attack, as shown by current density maps obtained by SVET (Fig. 2). This is specially pronounced on the galvannealled steel (Fig 2.b).



Fig 1: $i \ge E$ curves on Zn-based coatings at (a) 50 and (b) 1 mV/s.

Fig 2: *i*-maps (μA/cm²) obtained by SVET on (a)HDG Zn,(b) HDGA and (c) HDG Zn43AlSi.

In Situ Evolution of Non-Chromate Inhibitor Films by Simultaneous Neutron Reflectivity and Electrochemical Methods

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Environmentally friendly conversion coatings based on trivalent chromium, cerium and zirconium compounds are candidates to replace chromate, Cr(VI), in metal-protective applications. Currently, however, elucidation of inhibitor mechanism is compromised by the heterogeneity of structure, composition, and local solution conditions at the metal surface. To circumvent ambiguities introduced by these factors we utilize neutron reflectivity (NR) together with electrochemical methods to determine the structure, speciation and anti-corrosion mechanism of non-chromate inhibitor systems.

The in-situ approach is based on a galvanic liquid cell that separates the anodic and cathodic reactions on split metal-coated Si wafer substrates. Corrosion activity is measured electrochemically while simultaneously observing the evolution of interface morphology using NR. Specific corrosion scenarios are simulated by varying the electrode surfaces (metal and coating) and solution conditions (salt and inhibitor). By flipping the cell, both the cathode and anode surfaces are interrogated by the neutron beam. A series of NR snapshots of the active metal-solution interface is collected in the presence of the corrosion electrolyte.

We successfully determined the composition of both commercial and simplified Zr/Cr(III) hybrid conversion coatings. Well-defined Zr/Cr(III) inhibitor films were electrolytically deposited on Al-coated silicon wafers (anodic polarization to strip the oxide followed by cathodic polarization to trigger growth of the inhibitor film).

A Zr/Cr(III)-passivated Al anode was coupled to another passivated Al cathode (Fig. 1 a). The couple is exposed to neutral NaCl solution for 18 hours. NR snapshots of the anode show that the inhibitor films and Al layers are stable consistent with good performance of the Zr/Cr(III) system. We mimic a self healing scenario by raising the passivated Zr/Cr(III) anode to 20mV above open circuit potential and adding CeCl₃ to the cell. The current density profile shows that corrosion is induced initially, but decays over 24 h to zero. NR snapshots reveal that a new film species forms on the cathode simultaneous with the decline of the corrosion current. To our knowledge these are first real-time measurements of the evolution of an inhibitor film in a corrosion electrolyte.



Fig. 1. Galvanic cell for simultaneous neutron reflectivity and electrochemical measurements. The neutron beam penetrates the Si-wafer substrate. The cathode is interrogated by flipping the cell.

Self-Healing Anticorrosive Organic Coating Based on the Release of a Reactive Silyl Ester

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The easiest and mostly applied method to protect and to reduce corrosion rates of metals is the use of organic coatings which offer protection by active pigment release and passive barrier mechanisms. However, when these systems suffer any kind of damage the passive protection is no longer there and the metal substrate is directly exposed to the corrosive environment. Under these conditions, corrosion inhibitors, of which the most used and efficient ones are chromate-based pigments, are leached out from the coating and act at the metallic substrate. This mechanism is known as self-healing (SH) mechanism by inhibitor release. Intrinsic to this approach is that the pigment in the coating is released without control until there is no more pigment left in the coating. This leaves a depletion zone in the coating that does not allow further protection.

During the last decade, a different active SH mechanism based on the sealing of the crack-damage has been described and implemented to anticorrosive organic coatings. This second approach proposes the recovery of the barrier protection by the reaction of chemical species that are released from the coating or by the use of expandable phases which will close the crack. One of the problems of this approach is that the sealing of the crack can entrap water and corrosive agents between the newly created barrier system and the metal thus impelling undercoating corrosion processes.

A possible solution to these problems would be the use of a system that protects the metallic surface by reaction with water at the metallic surface creating a passive layer on top of the metal. In this work a new organic-based healing agent based on a silyl ester is presented and its synthesis and performance is described. The silyl ester was first tested as a repairing agent (assisted healing) and secondly encapsulated and incorporated into an organic matrix to study the autonomic self-healing properties of the complete system. A new high-throughput technique for healing agents' evaluation named multiwell was employed to determine the minimum amount of agent to heal a crack. In order to evaluate the healing ability of the silyl ester, Electrochemical Impedance Spectroscopy (EIS) is used and identified to be a key technique for the development and performance evaluation of self-healing anticorrosive organic coatings.

Investigation into the Corrosion of Steel under or near Grease Layers

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This paper describes the results of experimental work undertaken to study the corrosion of carbon steel under or near layers of different greases. Four different food-grade greases from two manufacturers were studied using two different approaches: electrical resistance probes and electrochemical impedance spectroscopy (EIS) probes consisting of two plate cross sections separated by a thin shim. The grease was applied to either cover the probes or on the side of the probes and the probes were exposed at different temperatures and different relative humidities. Two of the four greases studied were found to be corrosive in that uncovered steel exposed in a humid environment at elevated temperature near the greases corroded faster than a control case with no grease in the vicinity. The corrosion rate of the control case is similar to what would be expected for atmospheric corrosion whereas the corrosion rate of the steel exposed near grease is much higher than that for steel even in a severe marine environment. In contrast, the other two greases seemed to inhibit the corrosion of nearby unexposed steel. The corrosion rate of fully-covered steel was much lower, but could be assessed quantitatively by EIS. Despite severe challenges in using this method, the results clearly show that there is electrochemical activity under the greases. The rate of steel corrosion under one of the greases was about 10x lower than under the other greases. Samples partially covered by the aggressive greases exhibited corrosion that propagated from the uncovered region to the covered region, whereas the other greases did not exhibit this tendency. These data compare extremely well to other conventional corrosion rate measurements and field performance observations. The study shows how quantitative corrosion rate measurements can be made even in non-conductive environments that present a challenge to most electrochemical techniques.

Mechano-electrochemistry of Passive Surface Using *in Situ* Micro-indentation Test

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In situ micro indentation test was developed in order to investigate the mechanoelectrochemical behavior of passivated iron and aluminum. A couple of anodic current transients due to depassivation and repassivation of the surface in boric-borate buffer solutions under the potentiostatic condition were observed simultaneously with loaddepth curve of the electrode surface. The current intensity was strongly dependent on not only electrochemical conditions such as solution conductivity, electrode potential, and material's composition but also mechanical conditions including indenter driving speed, indent depth, and material's hardness. In the case of anodized aluminum, the current transients were also affected by thickness of oxide film and electric field applied to the film.

Depassivation and repassivation mechanisms were discussed from the electric charges during the loading and unloading of the indenter. The charge during the unloading was similar with or larger than that during the loading. The drive of the indenter accompanies the deformation of surface oxide film as well as substrate metal and leads to rupture of the film (depassivation). During the loading, although the ruptured area is partly covered with the indenter face driven further, the out side of the covered area exposes to the solution and repairs the oxide (repassivation). During the unloading, on the other hands, the area covered by the indenter can be exposed to solution and repassivated.

Because of significantly small thickness of the film formed on iron compared with the indent depth, variation of the ruptured area during the indentation with passivation condition was not obviously appeared, whereas the hardness of iron substrate affects the area to flow different depassivation-repassivation current. However, in case of the aluminum electrode, the film-ruptured area strongly depended on the film thickness when a same potential was applied to the film. Thus, the sufficiently thick oxide film formed on aluminum can restrict the corrosion mechanically.

In situ indentation was also applied to stainless steels in order to evaluate their corrosion resistance in highly concentrated NaCl solution and successfully demonstrated that type-312 stainless steel could be repassivated even after the indentation in 3.5 mol dm⁻³ NaCl solution at 323 K.
Preparation of anodization/SNAP film coated on magnesium alloy and study of its corrosion protection

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Magnesium and its alloys have unique advantages. Unfortunately, magnesium and its alloys have poor corrosion resistance due to their high chemical activity. Usually, the surface treatments are frequently used for corrosion protection of magnesium alloys. In this paper, an anti-corrosion bilayer was use to protect AZ31B magnesium alloy, which was made by first applying anodization to modify the magnesium alloy surface and subsequently depositing a SNAP (self-assembled nanophase particle) film. The results show that the bilayer was composed of a SNAP/loose layer and a dense layer. Both of them had contributed to the corrosion protection of the Mg substrate for more than 354 h in 0.005 M NaCl solution: the SNAP/loose layer was dependent on its good compactness, strong adhesion and high thickness due to the high density of the Mg-O-Si covalent bonds and Si-O-Si bonds in this layer. For the inner dense layer consisted of MgO and Mg₂SiO₄, it had better compactness than the SNAP/loose layer and inner dense layer during the immersion process, there was no large scale corrosion reactions occurred on the surface of Mg substrate.

Keywords: magnesium alloy, anodization, SNAP, corrosion protection

Corrosion Protection of Aluminum Alloys by Trivalent Chrome Process Treatment

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The Trivalent Chrome Process (TCP) has been widely used in industry recently as a metal pretreatment. This process is consider to be an environmentally friendly replacement for chromate conversion coating, because the TCP bath and the resulting film contain no chromate species. In our study, the mechanism of corrosion inhibition provided by TCP coatings has been explored.

Artificial scratch cells were used to test for chromium species of active corrosion inhibition on bare Al alloy substrate as a result of the release of inhibitors from coatings in close proximity, which are separated by a thin layer of electrolyte. Changes in corrosion resistance of both the bare surface and the coated surface were monitored by using electrochemical impedance spectroscopy. The bare surfaces were also examined for presence of chromium species and their oxidation states by using X-ray photoelectron spectroscopy.

Dilute Harrison's solution was used in this study. XPS analysis confirmed the presence of chromium species on the surface of the previously untreated AA2024-T3 sample after exposure in the artificial scratch cell. Fitting of the XPS spectra indicates that these species are mainly Cr(III), but that a small portion of Cr(VI) could be present. Accordingly, EIS measurements indicated an increase in the low frequency impedance of the bare surface resistance with time, which also suggests active corrosion inhibition derived from transport of chromium species from the treated sample through the electrolyte to the bare aluminum surface.

Transmission electron micrograph of TCP coatings was taken on matrix of AA2024-T3 milled by the focus ion beam (FIB). Relative uniform coating thickness in the range of 50~110 nm thick has been observed. Nano-EDS line profiling suggested that the coating is mainly composed of Zr, Cr, O and Al.

Crack Initiation on Alloy 690 in Lead-Contaminated High Temperature Pressurized Water

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The effect of scratch on crack initiation of Alloy 690 was investigated. The corrosion and stress corrosion tests of scratched Alloy 690 were conducted in lead-contaminated (10wt.% NaOH + 10g/L PbO) high temperature pressurized water (330°C, 15.6MPa). The fracture surface and the crass section were studied using scanning electrochemical microscopy (SECM) and scanning electron microscopy (SEM). The results showed that scratch caused residual compressive stress underneath the scratch, dissolution was preferentially active at scratches and intergranular cracks initiated at the bottom of scratch after immersion in caustic lead-containing high temperature water. At the macro-compressive stressed area, localized tensile stress caused by oxide jacking could initiate crack. Surface treatment like shot peening, if it is not properly applied, can be very harmful and cause stress corrosion cracking (SCC). No matter bulk stress is compressive or tensile, the localized tensile stress ahead of defects decides SCC.



Crack initiation at the bottom of a scratch

Electrochemical Characterization of Oyster Shell as an Environmentally Friendly Ceramic Coating Material

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The shell of the Eastern oyster (*Crassostrea virginica*) is composed of multiple incongruent mineralized layers that are manufactured by the organism in a cellular mediated process (Figure 1). This bioceramic composite material was investigated to determine its electrochemical behavior using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) and scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS). SEM-EDS analysis of the oyster shell revealed that the multilayered biocomposite material is composed of calcium carbonate (CaCO₃). EIS measurements in 3.5 wt% NaCl indicated that the impedance of the whole and intact oyster shell in the low frequency region exhibited high impedance values which exhibited a decreasing trend with increasing immersion time Figure 2). In terms of overall shell thickness, current densities measured by potentiodynamic techniques through the shell immersed in 3.5% NaCl were observed to increase when the outer layers of the shell were sequentially removed by grinding, thus decreasing the shell thickness; current densities were observed to remain constant when the inner



layers of the shell were removed with decreasing inner layer thickness. The impedance of the oyster shell material as measured by EIS were shown to decrease with decreasing shell thickness. These results suggest that this naturally occurring biocomposite ceramic may be suitable as a coating material for materials where corrosion resistance, wear and thermal protection are a concern.

Figure 1. Scanning electron micrograph of exterior shell layers with shell thickness in 3.5 wt% NaCl solution

Figure 2. Impedance variation of interior and a cross-section image of an oyster shell.

Formation of Localized Corrosion-Relevant Surface Defects on Aluminum - Experimental Studies and Kinetic Monte Carlo Simulation

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Near-surface microvoids in Al metal can function as pit initiation sites, as the oxidefree void surface is highly reactive when exposed during uniform corrosion.¹ Indeed, large void populations are produced by alkaline dissolution pretreatments used to enhance rates of pit initiation during industrial etching processes. The origin of interfacial voids and their potential relevance in initiation mechanisms of localized corrosion was explored through experiments in combination with Kinetic Monte Carlo simulations. In earlier work, it was found that alkaline dissolution treatments result in formation of aluminum hydride, along with elevated hydrogen concentrations in the near-surface region.²

We report in situ stress measurements on Al thin films during alkaline dissolution, using the wafer curvature method. A rapidly increasing tensile stress was observed, far in excess of that attributable to the removal of residual compressive stress in the film. The stress increase was accompanied by mass loss detected by QCM, and its onset coincided with the formation of aluminum hydride at the metal-oxide interface, detected by SIMS and potential transients.² The tensile stress increase also immediately preceded the period of rapid void formation identified previously by positron annihilation spectroscopy and TEM. The tensile shift is explained by the lattice contraction accompanying formation of hydrogen-vacancy (H-Vac) defects by dissolution, triggered by the appearance of hydride at the oxide-metal interface.

A Kinetic Monte Carlo (KMC) simulation of alkaline dissolution is presented which successfully rationalizes these experimental observations. The simulation follows electrochemical nucleation and growth of hydride islands at the metal-oxide interface, and also includes transport processes in the subsurface metal region. The simulation incorporates the hypothesis that H-Vac defect formation occurs preferentially at the island perimeter. The simulation successfully predicts observed formation of gas-filled voids (by H-Vac aggregation), interstitial H (by absorption from the void surfaces), and hydride particles within the metal. The principle governing H-Vac formation may also apply at the perimeters of preexisting cathodically active phases such as intermetallic particles or impurity clusters, and could explain the widely observed tendency of these sites to initiate localized corrosion.

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Oral Presentations

Simulation of Electromagnetic Response (EIS) of Corrosion Protective Coatings to Flaws

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Interpretation of electrochemical impedance spectroscopy response of corrosion protective coatings is frequently accomplished applying equivalent circuit element analysis. Equivalent circuit analysis is often more of an art than mechanistic science. requiring addition of various linear and nonlinear circuit elements to represent the spectral response of the material. The interpretation of the elements is based upon experience and faith, since the EIS response is averaged over a significant area which may or may not be homogeneous. The physical elements associated with the equivalent circuit element span length scales from nanoscale through micron scale and beyond. The advent of multiphysics finite element simulation tools has allowed testing of conceptual processes associated with equivalent circuit elements to be evaluated numerically. These numerical simulations have illuminated and even quantified, such effects as the water inclusion shape on the capacitance, for a given water volume fraction. The impact of water advance during the EIS measurement has been shown to produce equivalent circuit elements such as the constant phase element. These aspects of simulations and other advances will be discussed. Continued investigation of EIS spectra by simulating various proposed physical configurations of the coating and measurement system is likely to continue offer physical insights into processes associated with coatings protection and degradation, and when used in combination with physical and chemical measurements lead to more reliable coating protective lifetime prediction.

A proposed model for coated steel exposed to simulated soil environments by integrating mechanistic and statistical approaches

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Different life prediction models for steels with and without coatings have been analyzed using mechanistic models to predict durability in buried conditions with good approximation. The statistical approach is gaining more attention due to the stochastic nature of the corrosion process (e.g. pitting) with external surrounding parameters. In this work we present electrochemical monitoring results for different steel coated samples simulating soil conditions by using electrochemical impedance spectroscopy (EIS). EIS is used to quantify "in real time" the state of the interface (coating/ steel /electrolyte) and generate important parameters related to the degradation of the coating and describes the corrosion mechanism. Semi-empirical expressions are used to integrate the statistical stochastic nature of the corrosion process with the parameters and the mechanistic phenomena.

Effects of Selected Water Chemistry Variables on Copper Pitting Propagation: Experiments and Modeling

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Pitting corrosion is one of the major forms of copper tubing failures in potable water distribution system. In this study, the pitting propagation behavior of copper (UNS C11000) was investigated from an electrochemical perspective using the artificial pit method. Pit growth was studied systematically using a range of dilute HCO₃⁻, SO₄²⁻ and Cl⁻ containing-waters at various applied potentials. Pit growth was consistent with Ohmic-controlled propagation at intermediate potentials and mass transport control at high potentials. However, pit growth rate was independent of the bulk solution conductivity. Instead pit propagation was mediated by the nature of the corrosion products formed both inside and over the pit mouth (i.e., cap). Certain water chemistry concentrations such as those high in sulfate were found to promote fast pitting that could be sustained at low applied potentials. In contrast, Cl⁻ containing waters without sulfate ions resulted in slower pit growth. High HCO₃⁻ concentrations relative to Cl⁻ or SO_4^{2-} suppressed pitting. These observations were interpreted through understanding of the type and amount of corrosion products formed inside and over pits as well as their resistive nature. Specifically high [SO₄²⁻]/HCO₃⁻] ratio waters formed mainly brochantite corrosion products. These pits experienced increased propagation rates that became incrementally slowed over time but did not repassivate. In contrast, sulfate free waters at various [Cl⁻]/[HCO₃⁻] ratios resulted in lower pit propagation rates at all potentials. Long term stifling and repassivation occurred in these waters. Modeling work was performed at Swerea-Kimab using finite element software. A cylindrical pit geometry was assumed. A potential was applied between the mouth of the pit and the actively corroding pit bottom. The model included copper oxidation kinetics, transport by migration and diffusion, Cu(I) and Cu(II) solid corrosion product formation governed by equilibrium thermodynamics and a saturation index, as well as pit current and depth of penetration. Malachite, nantokite, cuprite, bronchantite and atacamite corrosion product formation was considered as governed by the conditions inputted and ion accumulation. Stifling was predicted based on a decrease in pit current assuming a corrosion product resistance proportional to film thickness and porosity. The findings of the modeling were in good agreement with artificial pit experiments. The ramifications of these finings towards pit propagation in potable waters will be discussed. Moreover, possible mitigation of on-going pitting by alterations in water chemistry during pit propagation will also be discussed. This is the type of practical research that provides direct practical benefit to various stakeholders such as home owners, water treatment facilities and copper tubing manufacturers. This type of work was the hallmark of Fontana's career.

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Investigation of Environmental Effects on Intrinsic and Galvanic Corrosion of Welded Carbon Steel in CO₂ Environments

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Localized corrosion of carbon steel welds has been thought to arise primarily from galvanic effects due to compositional differences between weld metal, parent metal and heat affected zone (HAZ) induced by the welding process. The location and morphology of the preferential corrosion is influenced by a complex interaction of environmental parameters. In the present study, additions of H₂S, inhibitor, acetic acid, and their combinational effects were investigated by using electrochemical techniques, such as linear polarization resistance (LPR) and galvanic current measurements. Intrinsic corrosion rate (uncoupled) was measured by LPR whereas galvanic corrosion rate (coupled) was calculated from the galvanic current. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and infinite focus microscopy (IFM) were applied to characterize the surface morphology and the chemical composition of corrosion products. The test results showed that the addition of 50 ppm H_2S and/or 20 ppm inhibitor reduced the intrinsic corrosion rate of weld segments (weld metal, parent metal and HAZ) and lead to lower galvanic corrosion rates between different weld segments, compared with that observed in the CO₂ environment. The addition of acetic acid under the same conditions increased the intrinsic corrosion rate of all weld segments and lead to higher galvanic corrosion rate.

Application of Electrochemical Impedance Spectroscopy for the Study of Under Deposit CO₂ Corrosion of Mild Steel

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Electrochemical techniques including linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) were applied to investigate the mechanisms of under deposit CO₂ corrosion of mild steel. Initial testing was directed towards defining and modeling the fundamental mild steel CO₂ corrosion mechanisms occurring under inert solid deposits with different particle size and shape (SiO₂ powder, glass beads and sand). Experiments were conducted in 1 wt% NaCl electrolyte for 24 hours at a CO₂ partial pressure of 0.96 bar (25°C) and 0.54 bar (80°C) respectively. Solution resistance, charge transfer resistance and diffusion resistance were able to be separated by using EIS with scanning frequency from 1 kHz to 1 mHz at open-circuit potential. It was also found that EIS predicted general corrosion rate of mild steel under deposit on charge transfer and mass transfer processes of CO₂ corrosion, as well as on the formation of corrosion product could also be identified. It was proved that the EIS technique has great utility than LPR and of great potential for under deposit CO₂ corrosion study.

Electrochemical Noise Analysis to Determine Critical Pitting and Crevice Temperatures in Simulated Sour Environments

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The critical pitting and crevice temperatures (CPT and CCT, respectively) of corrosion resistant alloys (CRAs) are commonly used as design parameters in the materials selection process. However, CPT and CCT standard procedures such as ASTM G48 and G150 use highly corrosive environments or very aggressive potentiostatic anodic polarizations above the pitting potential, which does not mimic service conditions and could lead to erroneous decisions.

In this work, electrochemical noise (ECN) analysis was used to determine the pitting corrosion susceptibility of conventional 13-Cr (L80-13Cr) and super 13-Cr (S13Cr-95) martenstic stainless steels as well as 22Cr and 25Cr duplex stainless steels, in simulated production environments with and without 850 ppm of $H_2S(g)$ and 1.7% $CO_2(g)$ at elevated pressures.

In contrast to similar experimental arrays, samples remained at their free corrosion potential for most of the test duration except for intervals of 1024s in which ECN measurements were conducted. Temperature was increased stepwise from 25°C to 200°C after each ECN block. During ECN measurements potential and current fluctuations were recorded using a zero resistance Ammeter (ZRA) under steady state conditions. The ability of ECN to differentiate between different corrosion mechanisms was also investigated on model systems.

Managing High Temperature Corrosion in the 21st Century

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This presentation summarizes generalized strategies to organize and to exploit data on gas phase corrosion of metals and allovs. These approaches are used in oil refining. petrochemicals production, power generation, energy conversion, chemical processes, propulsion and heated processes. Databases were developed to manage 15.4 million hours of exposure times for 100 commercial alloys at temperatures of $200 - 1,200^{\circ}$ C. The corrosion data and the resulting corrosion predictions consider total metal penetration. which includes surface recession and subsurface corrosion. Thermochemical predictions of corrosion product phase stabilities for phases formed from Fe-Ni-Cr-Co-C-O-S-N-H-Cl consider all known phases based upon combinations of these elements to allow rigorous assessments of corrosion product stabilities. These corrosion product stability predictions are used to suggest the likely dominant corrosion Previous thermochemical calculational approaches used simple mechanisms. assumptions of pure component corrosion products and alloy components. This technology considers real corrosion product phases and alloy compositions and is used in corrosion research, alloy development, failure analysis, lifetime prediction, selection of materials/alloys for equipment fabrication, equipment maintenance scheduling, and The corrosion mechanisms discussed in this process operations evaluations. presentation are oxidation, sulfidation, sulfidation/oxidation, carburization, nitridation, chlorine/HCl corrosion, metal dusting, nitridation and cyclic oxidation.

Key words: oxidation, sulfidation, sulfidation/oxidation, carburization, nitridation, ASSET, high temperature corrosion, and corrosion engineering lifetime prediction

New Findings on Intergranular Corrosion Mechanism of Ti-stabilized Ferritic Stainless Steels

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It is generally accepted that intergranular corrosion (IGC) of the stabilized stainless steels is induced by the chromium (Cr) depleted zone due to precipitation of Cr-carbide along the grain boundary. However, it is observed that IGC of Ti-stabilized ferritic stainless steel (FSS) is induced by Cr depletion due to Cr segregation adjacent to TiC precipitation along the grain boundary, but not due to precipitation of grain boundary Cr-carbide.

IGC and precipitation behavior of FSS were investigated with change in Cr content from 11 wt.% to 17 wt.%. IGC resistance of 11 \sim 13 wt.% Cr FSS was examined by free-exposure corrosion test using a modified copper acid sulfate solution. IGC occurred in the specimens aged at 400, 500 and 600°C, but not at 700°C. The sensitization time decreased with increasing aging temperature and the sensitization nose was positioned around 600°C. Increase in Cr content improved IGC resistance as the temperature and time for sensitization became higher and longer, respectively, but did not prevent IGC completely.

A transmission electron microscopy (TEM) and an energy dispersive X-ray spectroscopy (EDS) analysis were conducted on the intergranular precipitates in $11 \sim 17$ wt.% Cr FSS. The intergranular precipitates in all specimens where IGC occurred were identified as TiC with a face centered cubic structure having lattice parameter of 0.433 nm, and Cr peak was also detected by EDS analysis on the precipitates. Furthermore, no second phase such as carbide or intermetallic phase containing Cr was detected by TEM and EDS analysis. Analysis by a laser assisted three-dimensional atom probe (3DAP) characterization showed a strong segregation and resultant depletion of Cr atoms along with segregation of C and Ti atoms along the grain boundary in the specimen suffered from IGC.

Based on TEM, EDS and 3DAP analyses on the precipitates and atomic distribution around the grain boundaries, this study provides a critical information about the IGC mechanism of Ti-stabilized FSS containing low content of C and N. Regardless of Cr contents, IGC of Ti-stabilized FSS is induced by the Cr depletion due to the intergranular segregation of Cr adjacent to fine TiC precipitates, but by the Cr depletion due to formation of Cr-carbide and/or Cr-nitride which are generally known as the main cause of IGC in FSS.

Life Prediction and Field Corrosion Behavior of Stainless Steel for Automotive Mufflers

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The life time of the automotive exhaust system has been extended longer than two years in the world for recent ten years. Car makers have upgraded the materials of this system to certify the quality and to save the cost both. One of the major parts of this system is a muffler where the exhaust noise should be reduced. The life time of muffler can be mostly determined by the internal corrosion which is caused by the condensed water. Stainless steels have been used as the materials of muffler for longer than 30 years because of their excellent corrosion resistance. Recently, high-Cr stainless steels have been applied in this field to guarantee the extended warranty period. Typical grades of stainless steels in this application were type 409L stainless steels(11 wt.% Cr), type 439 stainless steel(17 wt.% Cr), and type 436L stainless steel(17 wt.% Cr-1 wt.% Mo). The internal corrosion of muffler has been issued in South Korea. Sometimes, the perforation on the muffler shell happened in the warranty period, which is caused by the acidic environment of condensed water in muffler. Car maker and materials supplier tried to establish the guidance to select the proper materials of each part. The corrosion resistance of several stainless steels was evaluated in the lab-made synthetic condensed water with different ionic concentrations. The test solution were composed of chloride ions of 50 ppm through 300 ppm, sulfate ions of 1000 ppm through 3000 ppm, sulfite ions of 500 ppm through 2000 ppm, and pH of 2 through 8. The passivity of the stainless steels was very sensitive to pH level and the contents of sulfur compounds. Most of stainless steels showed active dissolution behavior in low pH and highly sulfate-containing environments. Muffler can operate at high temperature up to 400°C. The oxidation is another mechanism to degrade the materials and it can accelerate the corrosion attack by the synergistic reaction. The oxide scale formed on the stainless steels supply the crevice site between the scale and metal matrix where the localized attack is initiated. Also, chromium is depleted in the matrix below the oxide layer, which decreases the corrosion resistance of the surface of stainless steels. In this paper, the effects of the ionic compositions in condensed water and of the oxide scale on the corrosion of stainless steels in corrosion environment of muffler were studied and the quantitative guidance is suggested to recommend the proper materials for muffler application.

Corrosion characteristics of Powder Metallurgy (P/M) aluminum alloys

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The ever growing industry of Powder Metallurgy (P/M) is developing new alloys and improve those currently available. One such alloy is the commercially available Al-Zn-Mg-Cu based alloy (Alumix 431D) which is the P/M equivalent of the wrought 7075 alloy, and yields some of the top performance found in any available aluminum alloy. However, its corrosion characteristics are largely unknown due to the uncertainty caused by the surface porosity. This is also true for all P/M alloys. In this work Cr was added in trace amounts in an attempt to improve the corrosion resistance. The corrosion resistance was studied and compared to the wrought 7075 equivalent. For 'as-sintered' P/M components the Tafel extrapolation was less effective in accurately determining corrosion rate due to the effect of porosity on surface area. To remedy this, samples were hot worked to near full density (>99.5 % theoretical), heat treated and re-tested. The hot worked P/M samples performed up to two times better than the wrought 7075 with respect to corrosion current densities. The effect of the surface porosity on the corrosion current densities.

Effects of Mn on the Localized Corrosion Behavior of Fe-18Cr Alloys

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Conventional austenitic stainless steels (γ -SSs) have been widely used as structural materials due to their advantage of excellent corrosion resistance and formability. However, production costs of conventional γ -SSs are high because they contain 8~12 wt.% of Ni, an expensive austenite stabilizing element. Therefore, high Mn-N SSs (Fe-(16~19)Cr-(1~4.5)Ni-(8~11)Mn-(0.2~0.5) N), in which Ni is replaced by cheaper austenite former, Mn and N, are being developed actively.

Mn is cheaper austenite stabilizing element than Ni, but it has been reported that the Mn addition causes a significant degradation of corrosion resistance of SS due primarily to the formation of MnS. However, the harmful effects of MnS on the resistance to localized corrosion have, recently, been significantly reduced using refining technology. Compared with extensive works on the effects of MnS on the localized corrosion of SSs, however, the inherent and independent effects of Mn on passivity and localized corrosion have rarely been investigated.

In this study, we examined the inherent effects of Mn on passivity, localized corrosion of Fe-18Cr alloys (Fe-18Cr-xMn (x=0, 6, 12)) with excluding the influence of MnS, using various electrochemical tests such as micro-droplet cell test and EIS.

As Mn content increased, the degradation of the passivity of Fe-18Cr alloys was confirmed by the decrease in the pitting potential and the increase in the passive current density in polarization curves measured in 0.1 M NaCl solution. Metastable pitting behavior of the alloys was also investigated by electrochemical noise analysis (ENA). As Mn content increased, the frequency of occurrence as well as the magnitude of the current spikes increased, suggesting that the susceptibility to metastable pitting of the alloys increased with Mn content. Considerable number of pits occurred at the edge of manganese-oxide type inclusion, indicating that manganese-oxide type inclusion also acts as a pit initiation site, although it may be less harmful than MnS. To examine the effects of Mn on the inherent protectiveness of passive film with excluding the influence of any NMIs (nonmetallic inclusions), we used the electrochemical microdroplet cell technique. The inclusion-free microregion of Fe-18Cr was immune to pitting corrosion up to 1.2 V in 0.1 M NaCl solution. However, the inclusion-free region of Fe-18Cr-12Mn was susceptible to pitting corrosion at 0.4 V, demonstrating that pitting susceptibility of passive film was significantly reduced by the addition of Mn even though NMIs were not included in the probe area.

To examine the effects of Mn on the pit propagation behavior of SSs, the active dissolution kinetics of Fe-18Cr alloys were investigate in an acidified chloride solution that simulated a pit internal environment (0.1 M HCl solution), using EIS. From the results, it was analogically inferred that Mn facilitates the metal dissolution inside the pit by enhancing the activity of iron adsorbed intermediate acting as a dissolution path. Moreover, Mn would delay the repaasivation process by reducing the activity of passivating species, i.e. chromium adsorbed intermediate.

Effects of AC on Passive Metals Corrosion

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Alternating current enhanced corrosion has been considered since the beginning of the XX century. Despite the increased number of scientific publications in the last two decades, AC-induced corrosion continues to be a controversial subject and a full agreement on influencing parameters and interpretation has not yet been achieved. The mechanism by which AC affects the corrosion process is not yet understood: different theories and hypotheses have been proposed, but none of them is able to fully explain and describe such a phenomenon.

AC interference may increase corrosion rate of interfered metals by 3 to 5 times. Cases of AC-induced corrosion are reported also in the presence of cathodic protection (CP) system.

No experimental study has been performed on the influence of AC on passive metals, such as stainless steel in neutral solution, carbon steel in concrete or carbon steel structure under CP (due to cathodic current the local pH at the interface soil-steel is higher than 10, so carbon steel is in passive condition).

The influence of AC-induced interference on the localised corrosion resistance of passive metals is discussed on the basis of laboratory test results. Tests were performed in two conditions:

- AC interference on stainless steel specimens with different chemical composition in neutral solution varying AC density, chlorides concentration and surface condition. Potentiodynamic tests were also carried out to analyse the effects of AC interference on passivity current density
- 2) AC interference on carbon steel rebar in alkaline environment in the presence of chlorides. Applied AC was in the range of 10 A/m^2 to 500 A/m^2 .

Results allow to evaluate the effect of AC on: time-to-corrosion, critical chloride threshold, AC critical current density and corrosion morphology.

Pietro Pedeferri's Great Contribution on Understanding Corrosion in Concrete

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Pietro Pedeferri devoted his research activity during his long academic career at Politecnico di Milano on a wide range of corrosion and corrosion prevention fields. Efforts regarded passivation of valve metal such as titanium, then achieving a smart and intriguing method for its colouring through electrochemical anodic passivation, cathodic protection in offshore applications, localised corrosion of active-passive metal alloys. Among these activities, he started to investigate corrosion and protection conditions of steel embedded in concrete, when exposed to chloride-containing environment or carbonated, as well as the behaviour of stainless steels. This paper will address the main steps of Pietro Pedeferri's activities in this field, underling the decisive contribution for the understanding of the behaviour of steel in concrete. Cathodic protection of reinforcing steel in concrete structures was one of his main interest that lead to many industrial applications on structure with corroded rebars, first, then on new structures, not yet corroded, as a new preventative methods, he named "cathodic prevention". This was his original proposal which he accomplished to after a thorough study on implication of cathodic condition of passive steel, through the proposal of a new diagram, potential-chloride content diagram, which explained the behaviour of steel in concrete and allowed to understand the power of the application of cathodic protection to passive steel, i.e., cathodic prevention, before chloride contamination have being established.

Studies on Corrosion Characteristics of Fe-Cr Alloys and Sensitized STS 304 Using the Micro-droplet Cell Technique

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The corrosion characteristics of Fe-x Cr (x=17, 21%) alloys and sensitized STS 304 stainless steel were investigated in terms of influences of various parameters such as inclusions, surface roughness, exposed areas, Cr content, and the degree of sensitization using a micro-droplet cell. The micro-droplet cell technique allows an alignment of the micro-electrode to the desired spot of the working electrode and direct measurement of local currents with the electrochemical polarization. Microelectrochemical tests were applied to perform potentiodynamic polarization experiments on micro areas including inclusions, the inside of a grain and the grain boundaries. Results showed that some inclusions among oxides acted as initiation sites for the pit initiation but others did not. The rougher surface and the denser chloride ion concentration offered the easier pit initiation sites, causing the more susceptible to pitting corrosion. Micro electrochemical polarization curves were compared between the inside of grain and the grain boundaries in the sensitized STS 304 stainless steel.



Fig. Schematic of micro-droplet cell (a) and an electrochemical set-up with micro-droplet cell installed in optical microscope (OM) (b).

Oral Presentations

A Mechanistic Model of Localized CO₂ Corrosion for Carbon Steel

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A transient mechanistic model is being developed to predict the localized CO_2 corrosion process for carbon steel. Various phenomena associated with $_{CO2}$ corrosion processes, such as mass transfer, chemical reactions, electrochemical reactions and solid film (FeCO₃) formation are taken into account in the model. Localized corrosion is assumed to occur by formation of a galvanic coupling between a small active surface (anode) and the surrounding pseudo-passive surface (cathode). Anodic dissolution rate is calculated from the "mixed potential" of the metal surface based on galvanic coupling theory. The model simulates water chemistry change, potential change and corrosion rate change as a function of time. Comparison of the results reveals that surface pH, potential and current density are interrelated. Simulation indicates rapid enrichment of dissolved metallic species at anode and corresponding pH increase upon localized corrosion. This is contrary to pit acidification observed for crevice corrosion of stainless and alloy. The implications of this behavior are discussed.

Corrosion of an Al-Mg-Si alloy under MgCl₂ Solution Drops

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The corrosion behavior of an Al-Mg-Si alloy under droplets of MgCl₂ solution was investigated using a Kelvin probe (KP). A 6µl droplet of 0.1 M MgCl₂ solution was placed on the sample surface, which was then exposed to an RH of 33% (in equilibrium with saturated MgCl₂ solution) or 75% (in equilibrium with saturated NaCl solution). The open-circuit potential (OCP) was monitored by the KP. Because the equilibrium humidity of the 0.1 M MgCl₂ is higher than 75%, the droplet height is decreased, and a thin MgCl₂ solution layer with a thickness less than 50 µm forms on the alloy surface. During the initial stage of exposure to 75% RH, the OCP repeatedly exhibits a sudden decrease and then recovery, which is associated with initiation and repassivation of metastable pits. After about 7.5 hours, the OCP lowers slowly and then maintains a stable low, which is associated with stable pitting corrosion. Interestingly, when the RH is held at 33%, which will force the MgCl₂ droplet to the saturation concentration, stable pitting corrosion is not observed up to 72 hours. Metastable pits are observed, but the number and rate are much lower than in that of 75% RH atmosphere. Key words: Al-Mg-Si alloy; pitting corrosion; Kelvin Probe

Oral Presentations

Chemical Characteristics of Material Surfaces Exposed to Ambient Coastal Marine Atmospheres

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The evolving chemical environments that develop on material surfaces exposed to natural atmospheres regulate the nature and rates of associated corrosion processes. Inert (Polytetrafluoroethylene (PTFE)) and metal surfaces (low carbon steel, AA2024-T3, and Ag) were exposed to ambient atmospheres at Coconut Island, HI; Carson, CA; and Point Judith, RI for 3 and 6 months. Thereafter, the surface environments were chemically characterized via extraction in deionized water of soluble constituents (including Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, HCOO⁻, CH₃COO⁻, (COO)₂²⁻, CH₃SO₃⁻, Na⁺, K⁺, Mg^{2+} , Ca^{2+} , and NH_4^+) and analysis by ion chromatography. Loadings per unit exposed surface area were calculated and ratios of analytes (Cl⁻:Na⁺, K⁺:Na⁺, Mg²⁺:Na⁺) were compared with those in surface seawater. Ratios of major sea-salt-derived constituents at Coconut Island were statistically indistinguishable from those expected based on the deposition of marine aerosol. The pHs of minimally diluted extracts (5 μ L) of aqueous surface films on paired samples were measured using an ion-sensitive, surface-effect field transistor. Preliminary results indicate that, on exposed inert samples, the deposition of acidified marine aerosols and the dissolution of acidic gases and precursors sustained acidic surface solutions. In contrast, on exposed silver samples, alkalinity produced via oxidation titrated deposited acidity and sustained alkaline surface solutions. Implications for the associated corrosion processes will be discussed.

A Multifunctional Sensor for In-situ Monitoring Corrosion of Steel Reinforced Concrete Structure

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The premature degradation of reinforced concrete structure due to the corrosion of rebar is one of the most serious problems in modern society. Various electrochemical methods have been applied to study and monitor the corrosion of steel in concrete¹⁻³. Corrosion process of steel in concrete is extremely complicated and influenced by many mutually influenced factors, a single measured parameter is usually difficult to correctly predict the corrosion state and safety for a reinforced construction. The passivity and corrosion activity of reinforcing steel in concrete largely depends on the pH and Cl⁻ concentration at the steel/concrete interface. We have developed a multifunctional sensor for in-situ following the environmental parameters of pH and Cl⁻ concentration in concrete, and monitoring the corrosion electrochemical parameters of $E_{\rm corr}$, $i_{\rm corr}$ and R_p . It has been employed in a river tunnel construction, and the in situ measurement (in Fig.1) indicates that the pH remains a high level and the Cl concentration is very low in the concrete, consequently, the steel keeps completely passive, with the corrosion positive $E_{\rm corr}$ (-0.3V) and high $R_{\rm p}$ (>2×10⁴ Ω). It is demonstrated, from the evaluations in both laboratory and field, that the combined probe is able to follow the pH and Cl- concentration in concrete, and to monitor the corrosion state and corrosion rate of the rebar steel in concrete, providing more complete and correlative parameters for a correct and reliable prediction of the corrosion and safety for a steel reinforced construction.



Fig.1 In situ corrosion measurement for a tunnel construction (a), variation of pH and Cl⁻ concentration in concrete with time (b), and variations of E_{corr} and R_p of rebar in concrete with the service time (c).

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Local Passivation Breakdown of Carbon Steel in Bioethanol during Stress Corrosion Cracking

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Stress corrosion cracking (SCC) has been widely reported as a potential failure mode for carbon steel in ethanol environment. Both phenomenological and mechanistic investigations have been carried out to understand SCC of carbon steel in fuel-grade ethanol (FGE) in recent years. In this contribution, we report our recent investigations towards understanding the local passivation breakdown of X-65 carbon steel in simulated fuel-grade ethanol (SFGE) during the cracking process. Both *dc* and *ac* electrochemical techniques were applied to present physical details about the cracking dynamics. The results indicated that the growth of surface film as well as its breakdown presented a close relationship to the SCC initiation and growth. The corrosion activity ahead of crack tip controlled the crack propagation. A competition between active anodic dissolution and repassivation existed on the surface. A transition from SCC to pitting corrosion was also observed due to the change in ethanol chemistry. The role of ethanol chemistry on the localized corrosion will also be discussed to some extent. An EIS model will be developed to present a physical picture about crack growth in this environment.

Investigation of Stress Corrosion Cracking of Alloy 800 in Neutral Crevice Solutions

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Stress corrosion cracking (SCC) of steam generator (SG) tubing in SG second side crevice environments has been a major concern during the service of nuclear power generating systems. SCC is found mostly at the heat-transfer crevices associated with tube supports, where the impurities in the SG feedwater are highly concentrated in the SG crevices and result in an aggressive environment. The occurrence of SCC in a passive system is normally considered to be related to the breakdown of the passive film.

In this work, the impacts of impurities in SG crevice solutions on passivity and SCC of Alloy 800 were investigated. The fracture ductility of anodic films was measured for Alloy 800 at 300°C in a neutral crevice solution with various contaminations. The contaminations altered the film fracture ductility, the compositions of anodic films significantly and the effects of contaminations depended heavily on the impurity concentrations. The film rupture ductility correlated well with the stress corrosion cracking (SCC) resistance. Anodic films containing more M-OH and M-OH₂ bonds displayed lower film rupture ductility and higher SCC susceptibility. An increase in the Cr-content due to the presence of Pb contamination is unlikely to improve the passivity. The SCC of Alloy 800 is likely related to film rupture at the crack tip and that the high SCC susceptibility in the contaminated environments may be related to the reduced rupture ductility of anodic films. The donor densities of passive films on Alloy 800 formed in high temperature neutral crevice chemistries have good correlations with amount of M-OH bonds in the passive films and the SCC susceptibility. The experimental evidence indicates that there is a critical donor density in the passive film for SCC. Above this critical value, the SCC susceptibility increased rapidly with increasing donor density.

The Electrochemistry of Stress Corrosion Cracking

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Stress corrosion cracking of metals and alloys in aqueous environments is primarily an electrochemical phenomenon falling within the realm of the differential aeration hypothesis (DAH). As such, the local anode and the local cathode are spatially separated, with the former existing within the crack enclave (on the crack flanks and at the crack tip) and the latter existing on the bold, external surfaces. The resulting current that flows from the local anode to the local cathode implies strong electrochemical coupling between the crack internal and external surfaces and this coupling, which has been examined experimentally in a variety of systems, including intergranular stress corrosion cracking in sensitized Type 304 SS in water at 288 °C and in thiosulfate solution at ambient temperature, and hydrogen-induced cracking (HIC) in tempered martensitic AISI 4340 high strength steel in concentrated NaOH. In all three cases, the microfracture events are found to be much larger than can be accounted for by the slip-dissolution model and it is concluded that, in these cases, crack advance occurs by HIC. Furthermore, the crack length is predicted theoretically to exert a strong influence on crack growth rate in sensitized Type 304 SS in BWR primary coolant environment, because, as the crack grows, a larger fraction of the potential drop between the crack tip and the external surface appears as IR potential drop down the crack and hence less potential drop is available to drive the reactions that consume the coupling current on the external surfaces. Consequently, the magnitude of the coupling current drops as the crack lengthens and hence so does the crack growth rate. In is argued that, in this latter case at least, and possibly in all cases examined here, the rate of crack growth is controlled by the kinetics of the reactions that occur on the external surfaces and not by the events that occur within the crack.

Self-healing Coatings for Magnesium Alloys

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This presentation will report our achievements in designing self-repairing high performance environmentally-friendly coatings technologies for magnesium alloys used in automotive and aerospace applications.

Aluminum and its alloys are used widely in transportation, architectural, lithographic and packaging applications. The demand for weight savings for automotive and aerospace materials has focused attention on magnesium alloys.

Magnesium alloys have a variety of excellent properties, including a high strength-toweight ratio, low density, dimensional stability and castability. Therefore, several automobile manufacturers have co-operated to develop new magnesium alloys for manufacturing less energy-consuming and hence, less polluted automobiles. However, Mg alloys remain very susceptible to corrosion despite their excellent mechanical properties.

Chromate has been reported as the most efficient widespread conversion coatings for the corrosion protection of many metallic substrates. However, the waste containing hexavalent chromate has many limitations due to the environmental consideration and health hazards.

This presentation will discuss the recent research achievements in designing of selfhealing eco-friendly coatings based on cerate, stannate, zirconate and molybdate conversion coatings for different magnesium alloys.

The Corrosion Resistance of Anodized Aluminum 6061 during Long-Term Exposure and after a Thermal Cycling Treatment

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The long-term corrosion resistance of anodized Al 6061 produced by a hard anodizing process using a mixed acids solution (H_2SO_4 and $H_2C_2O_4$) was evaluated using electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The EIS data revealed that there was very little change of the corrosion resistance provided by the anodized layers during exposure in 3.5wt% NaCl for one year. The protective properties of the anodized layers for two different types of anodized Al 6061 samples that were subjected to thermal cycling treatments at 120, 160 and 200°C were evaluated using EIS and SEM. In this study one type of anodized Al sample was produced by the standard hard anodizing (type III) process. The other type of sample was anodized in the mixed acid solution. All samples were sealed in hot water. The thermal cycling treatment produced considerable damage of the porous layer and the barrier layer. The EIS data suggested that some cracks extended through the porous layer and the barrier layer into the bare metal. The open-circuit potential of these samples was close to that of bare Al 6061. The damage of the oxide layers increased with increasing thermal cycling temperature for both types of samples. Selfhealing of the porous layer and the barrier layer occurred during immersion in NaCl.

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The Effects of Water Vapor and Hydrogen on the High-Temperature Oxidation of Alloys

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Essentially all alloys and coatings and non-oxide ceramics that are resistant to corrosion at high temperature require the formation of a protective (slowly-growing and adherent) oxide layer by a process known as *selective oxidation*. The fundamental understanding of this process has been developed over the years for exposure in pure oxygen or air. However, the atmospheres in most applications contain significant amounts of water vapor which can greatly modify the behavior of protective oxidation. Two of the most serious effects of water vapor or steam on the high temperature oxidation of alloys are the increased spalling tendencies of Al_2O_3 and Cr_2O_3 layers, and the increased volatilization of certain oxides. Recently, it has also become apparent that the presence of water vapor can directly alter the selective oxidation process.

This talk will begin with a brief review of the fundamentals of selective oxidation followed by a description of recent experimental results regarding the effect of water vapor in atmospheres typical of those in gas turbines and solid oxide fuel cells (SOFCs). The topics to be discussed include:

- i. Water vapor effects on the selective oxidation of alloys containing Cr or Al.
- ii. Dual atmosphere effects in SOFCs.
- iii. Effects of water vapor on scale spallation.

The talk will conclude with a brief presentation of some rather surprising results in which exposure of an Fe-Cr alloy to water vapor affected the formation of sigma-phase on grain boundaries in the alloy.

Stochastic Modeling of Pitting Corrosion in Aluminum Alloys

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Any time development that can be analyzed in terms of probability is named a stochastic process, whether it is deterministic or purely probabilistic. Considering localized corrosion as a stochastic process is not a new concept¹ and stochastic theory was successfully used to explain pitting corrosion characteristics such as the probability distribution of both the pitting potential and the induction time². Adding deterministic aspects has also been shown successful in describing the effect of the applied potential, the chloride concentration or the microstructure on the pit generation rate². To our knowledge, only Shibata³ tried to apply stochastic theory on aluminum.

Using the work by Henshall et al.⁴ as a starting point, a framework was designed to develop and validate a phenomenological Monte Carlo-based model to predict pitting initiation and pitting growth processes in aluminum alloys. Experimental input parameters such as pit initiation, death and growth rates and also induction time were obtained from noise and potentiostatic measurements on 7075-T6 alloys. The influence of environmental factors such as [CI⁻], temperature or pH was taken into account by making the pit parameters dependent on these environmental factors. The influence of the microstructure was also considered. The validation was achieved by comparing pit depth distribution and pitted morphologies provided by the model with experimental data.

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The effects of droplet-surface interactions on the atmospheric corrosion of zinc

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Atmospheric corrosion is controlled by a complex mixture of variables including climatic factors, contaminant properties, droplet chemistry, and varied droplet-surface interactions with a metallic or coated surface. Contaminants that impact surfaces can lead to an array of droplet sizes and shapes, where the latter is controlled by the energetic properties of the surface.

In this work a coupled-multielectrode array of close-packed zinc wires was used to study the electrochemical current exchanges occurring beneath sodium chloride droplets. The square array was comprised of 500 μ m zinc electrodes and prior to droplet addition was exposed to a plasma cleaning process that varied the array surface energy, resulting in altered droplet contact angles. Seawater droplets in the range of 1 to 10 μ l were placed onto the array surface and were sustained at relative humidity exceeding 76% for 10 minutes before drying at decrease relative humidity over a further period of 20 minutes.

In agreement with the Evans droplet model of corrosion, increased anodic reactions occurred on the electrodes towards the centre of the droplet whereas cathodic reactions were increased towards the edges of the droplet. Both droplet size and surface energy influenced the magnitude of current exchange and most notably controlled the longevity of active corrosion. The trends in current exchange for individual droplets are discussed with respect to likely contamination and corrosion scenarios. Ultimately, the output from such work will provide a means to experimentally validate models for atmospheric corrosion.

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Conducting Polymer- Silica Nanoparticles based Hybrid Nanocomposites: A Facile And Green Synthetic Approach for Active Anti Corrosive Coatings

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Stainless steels (SS) are being increasingly used as a structural material in marine and petrochemical applications. This is mainly due to their high corrosion resistance, high strength and toughness. However, in the presence of chloride ions, localized corrosion such as pitting and crevice corrosion is still a serious problem for such materials. Hence, the study on SS in chloride media to enhance the corrosion protection has been a technological importance.

Development of a new generation of multifunctional coatings, which will possess not only passive functionality but also active and rapid feedback activity in response to changes in the local environment, is a key technology for the corrosion protection of SS in aggressive environment. These new multifunctional coatings should combine active and passive component, to provide fast responses of the coating properties in order to change the passive matrix of the coating (e.g., cracks, local pH change) and the local environment surrounding the coating (temperature, humidity). The coatings should also have several functionalities (e.g., antifriction and anticorrosion) exhibiting synergistic effects.

The present investigation demonstrates a new contribution to the design of a new protective system based on organic–inorganic hybrid nanocomposites composed of conductive Poly(orthophenylenediamine) (PoPD) and silica (SiO₂) nanoparticles through an *in-situ* chemical oxidative polymerization. The structure and morphology of the hybrid nanocomposites were characterized by transmission electron microscopy (TEM) scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction analysis (XRD) techniques. The anti-corrosion behavior of PoPD-SiO₂ hybrid nanocomposites has been investigated in 3.5% NaCl solution using potential-time measurements, potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) measurements. Electrochemical corrosion studies revealed that PoPD/SiO₂ hybrid nanocomposites coatings exhibited good corrosion resistance and long-term corrosion protection in comparison with the individual films. This improved protection provided by the coatings containing SiO₂ nanoparticles is attributed to the low porosity of PoPD/SiO₂ hybrid nano composites films by filling of the pores in the polymer by SiO₂ particles.

Atmospheric Corrosion of Silver and Its Relation to Accelerated Testing

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Understanding, recreating in the lab, and predicting atmospheric corrosion would be of great assistance to anyone whose materials or structures are exposed to the atmosphere. A first step in the development of the accelerated aging tests which would provide this information must be an understanding of the corrosive agents present in a given environment and their effects on the exposed material. In this work, silver is exposed to both field and laboratory conditions. Silver is usedbecause corrosion proceeds quickly on this metal, making it a good indicator metal. Also, the films produced are tenacious and reducible allowing the use of coulometric reduction for analysis of the corrosion products, both identifying the species produced and determining the amount produced. Field exposures showed that silver chloride and silver sulfide are common corrosion products and silver chloride is the main product from coastal exposures. Coastal corrosion rates were found to be higher than inland corrosion rates. Laboratory exposures controlled relative humidity, ozone concentration, and exposure to UV light. The presence of both ozone and UV illumination was necessary for corrosion for the limited exposure times here. The amount of corrosion was found to be independent of relative humidity, and the amount of corrosion varied linearly with ozone concentration. Acceleration factors for several sites are developed and compared. The kinetics of oxide formation is examined in various laboratory environments and the diffusion limiting thickness found.

Causes and mechanisms of localized CO² corrosion

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When compared to uniform CO^2 corrosion of mild steel, not nearly as much is known about localized CO^2 corrosion. The causes of localized CO/2 / corrosion defined in a broad sense are many, and they can be divided in to those that lead to localized corrosion on a macroscopic scale and those that lead to a localized corrosion on a /microscopic/ scale. The first group includes: poor or incomplete inhibition, water and/or solids separation in multiphase flow, flow disturbances and extreme multiphase flow conditions, localized condensation in wet gas flow, preferential corrosion of welds, ingress of oxygen, presence of organic acids, presence of H² and elemental sulfur. Many of these factors appear simultaneously. Localized CO² corrosion on a microscopic scale is often caused by galvanic attack or bacteria. The various mechanisms of localized CO² corrosion on both macroscopic and microscopic scale are discussed.

Science-Based Maps and Correlations for Stainless Steel

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Engineers are often surprised when corrosion scientists cannot tell them whether stainless steel will corrode or not in a given aqueous environment. The situation is not too bad for dilute sulfuric acid, but for halide environments there is a need for science-based maps or correlation equations that can play the same role for the environment as the 'PREN' approach does for the metal. In this presentation we will outline recent progress and remaining challenges in this field. We also comment on the outlook for injecting more science into the PREN approach itself.

The fundamental basis of any such modeling approach should be propagation-based, despite the risk of excessive conservatism that this entails. Contributions of J.W Oldfield, J.R. Galvele, N.J. Laycock and others will be used to develop and illustrate the mapping or correlation strategy.

Oral Presentations

Crevice Solution Chemistries Evolution of Nickel-Aluminium Bronze in 3.5% NaCl Solution

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The failure of a mechanical structure, such as aircrafts, marine vessels and highway bridges, can cause large economic loss, and even loss of life. However, few corrosion sensing systems are available for structural health monitoring due to a lack of in depth understanding and detailed knowledge of the evolving chemical processes occurring within a range of corrosion microenvironments. At Southampton, we have successfully used capillary electrophoresis (CE) methodologies, in addition to screen-printed platinum electrodes, to quantify the nanolitre corrosion solutions produced within a range of different crevice microenvironments, and to identify the key species that are indicative of crevice corrosion occurring [1,2]. In this paper, crevice solution chemistries evolution of nickel-aluminium bronze (NAB) for over six months immersion in 3.5% NaCl solution were reported, and the identified key ionic species produced in the crevice exhibited a characteristic of selected phase corrosion behaviour of NAB [3]. Based on the information obtained from CE analysis, a novel thick-film based electrochemical sensing system was developed and optimised for in situ crevice monitoring.

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The Role of Proton Reduction in Complicating the Crevice Corrosion of Titanium

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Crevice corrosion of titanium is the product of a concentration cell formed when the dissolved oxygen content of the electrolyte solution within the occluded confines of a crack or crevice is consumed, generating acidic, anoxic conditions within the crevice while generally passive but more oxygenated (cathodic) conditions prevail on the exterior titanium surfaces. The consequent low pH and low potential that develop within the crevice promote proton reduction in the crevice interior; thus titanium oxidation becomes coupled to two cathodic drivers: oxygen reduction outside, and proton reduction inside, the crevice.

Although external oxygen reduction always remains necessary to maintain the crevice corrosion against "losses" of H^+ through diffusive escape from the crevice or incomplete hydrolysis of Ti cations, the internal coupling of the proton reduction-metal oxidation/hydrolysis cycle can be remarkably efficient. Consequently, as much as 70-97% of the damage in a Ti corrosion crevice can be attributed to the coupling of metal dissolution to proton reduction; i.e. proton reduction is the main contributor to crevice corrosion damage on Ti.

Proton reduction on Ti in acidic solutions, as takes place within a corroding crevice, results in both hydrogen gas evolution and atomic hydrogen absorption into the bulk of The rate and other attributes of the latter process are important in the metal. determining the extent of corrosion and the time required for sufficient hydrogen to be absorbed to cause hydrogen-induced cracking (HIC). This paper discusses some of our observations on the details of proton reduction and hydrogen absorption on Ti. In particular, proton reduction and titanium hydride formation appear to initiate on catalytic intermetallic particles present in the titanium due to alloying or impurities (e.g. Ti_xFe , Ti_2Ni , Ti-Pd). The formation of a surface hydride also catalyzes the proton reduction reaction, but hinders hydrogen absorption into the metal. Modest enhancement of proton reduction accelerates coupled metal oxidation, but further augmentation of proton reduction can result in enforced passivation. The efficiency for hydrogen absorption as a result of crevice corrosion is generally about 5-8%, seemingly independent of the duration of the corrosion period, temperature, or chloride concentration in the electrolyte solution.

Nickel undercoat to Improve Chromium Electrodeposition of Aluminium Alloys

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The high strength to weight ratio of light metals and their alloys makes them good candidates for newer applications in the automotive, aerospace, construction, chemical, food processing and packaging manufacturing industries. Due to the favourable physical properties of aluminium and its alloys (density, strength to weight ratio, and cost), there is a growing demand for nickel / chromium plated aluminium components especially in the automotive and aerospace industries and also for other applications in a variety of industries. However, aluminium alloys are difficult to plate either by cathodic or electroless deposition due to the tenacious oxide layer present on their surfaces.

The study carried out here explores suitable methodologies for the successful pretreatment of sample aluminium alloys prior to chrome plating. Data will show sample pretreatment steps applying the zincating process to aluminium prior to nickel and chrome plating. Surface morphologies and structures of the various samples during processing would be characterized using a variety of surface analysis techniques such as Scanning Electron Microscopy, X-ray Photoelectron Spectroscopy, Energy Dispersive X-ray Analysis and X-ray Diffraction Analysis.

Overall, the conclusion from the study will show that successful chrome deposition on sample aluminium alloys is dependent on their systematic pretreatment with the modified alloy zincate process serving as precursor for nickel deposition and prior to chrome deposition. The chrome plated samples were also subjected to mechanical and hardness testing to confirm any evidence of buckling or delamination of the coated samples.

The Anodic and Cathodic Dissolution of Al Alloys by Atomic Emission Spectroelectrochemistry

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Atomic emission spectroelectrochemistry (AESEC) is a new technique for the characterization of material stability in an electrolyte [1]. The technique combines an electrochemical flow cell with downstream elemental analysis using an inductively coupled plasma atomic emission spectrometer. In this work, we have used AESEC to monitor the release of Al from 99.99% aluminum (1199 alloy) and the release of Al, Mg, and Cu from 2024 Al alloy in 30 g/l NaCl electrolyte. An example of an AESEC polarization curve of the 2024 alloy at pH 6.19 is given in the Figure 1. The total electrical current (J), and the Al, Mg and Cu partial elementary currents are given as a function of potential. The partial elementary currents are calculated from the downstream concentration using Faraday's law. Specific mechanisms of dissolution difficult or impossible to elucidate from electrochemical data alone - are here clearly identified. The **cathodic dissolution** of Al is observed between -1400 and -1000 mV. The selective dissolution of Mg is observed between -1200 and -600 mV. Finally at E > -500 mV, the detachment of copper rich particles is indicated as very rapid spectroscopic emission transients (peak width < 10 ms. In this presentation we will discuss the kinetics of these phenomena as a function of pH and alloy composition. The dissolution mechanisms will be discussed in terms of interfacial pH and galvanic coupling between phases.



Fig. 1 AESEC polarization curve of 2024 Al alloy showing the total current J and the partial currents of Al, Mg and Cu. Different dissolution phenomena are observed in different potential regions as indicated by the wavy arrows.

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Oxidation of SiC fiber-reinforced SiC matrix composites with a BN interphase

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SiC-fiber reinforced SiC matrix composites with a BN interphase were oxidized in reduced oxygen partial pressures of oxygen to simulate the environment for hypersonic vehicle leading edge applications. The constituent fibers as well as composite coupons were oxidized in oxygen partial pressures ranging from 1000 ppm O₂ to 5% O₂ balance argon. Exposure temperatures ranged from 816°C to 1353°C (1500°F to 2450°F). The oxidation kinetics of the coated fibers were monitored by thermogravimetric analysis (TGA). An initial rapid transient weight gain was observed followed by parabolic kinetics. Possible mechanisms for the transient oxidation are discussed. One edge of the composite coupon seal coat was ground off to simulate damage to the composite which allowed oxygen ingress to the interior of the composite. Oxidation kinetics of the coupons were characterized by scanning electron microscopy since the weight It was found that sealing of the coupon edge by silica changes were minimal. formation occurred. Differences in the amount and morphology of the sealing silica as a function of time, temperature and oxygen partial pressure are discussed. Implications for use of these materials for hypersonic vehicle leading edge materials are summarized.

Mathematical Models for Cathodic Protection of Pipelines

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Mathematical models used to design systems for mitigation of external corrosion of pipelines also serve to illustrate the role of current and potential distributions as it pertains to cathodic protection of pipelines. In addition, methods used to assess the condition of buried pipes will be used to illustrate the integration of comprehensive numerical simulation with techniques for assessment of pipe coating condition.

Cathodic Protection of Buried Structures

External corrosion is commonly mitigated by coating the structure with a high resistance film and by employing cathodic protection (CP) to protect regions that are inadequately coated or where the coating has degraded. Defects in the coating are termed holidays, and such holidays can expose bare steel. Our group has developed finite-element and boundary-element calculations for cathodic protection of coated pipelines with coating holidays that expose bare steel. These calculations, developed for the Trans-Alaska pipeline, were validated by laboratory experiments on full-scale sections of the Trans-Alaska pipeline. The development of boundary-element models was generalized to account for interactions between multiple pipelines, to account for stray current between independent CP networks, and to allow calculations for very long sections of pipeline. The resulting software was used during remediation of the Trans-Alaska Pipeline and design of a new gas field in the South China Sea. These simulations will be employed to illustrate the influence of current and potential distributions on the ability of a CP system, to protect a buried structure from corrosion.

Close-Interval Potential Surveys for Buried Pipelines

Regular inspections of buried oil and gas transmission pipelines, such as described in the NACE International Recommended Practice for External Corrosion Direct Assessment (ECDA), are required to ensure the integrity of the pipelines. The methodology behind ECDA relies heavily on close interval surveys of on-potentials (where the CP system is connected) and off-potentials (where the CP system is disconnected). The boundary-element simulations described above were used to simulate ECDA measurements and to identify general interpretation strategies. The approach presented illustrates the integration of comprehensive numerical simulation of current and potential distributions with techniques for assessment of pipe coating condition.

A Model for predicting oxidation kinetics of refractory diborides

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The life of the leading edge of hypersonic vehicles is determined by erosion and refractory diborides are the leading candidates for this application. A mechanistic model that interprets the transition in oxidation behavior of the diborides of Zr and Hf as the temperature is varied from 600°C to above 2500°C is presented. Available thermodynamic data and literature data for vapor pressures, oxygen permeability in boria, and viscosity of boria were used to evaluate the model. Transitions in oxidation mechanisms with temperature are shown to be important in rationalizing experimental data. Good correspondence was obtained between theory and experiments for weight gain, recession, and scale thickness as functions of temperature and oxygen partial pressure. The model points to key factors that govern the oxidation behavior of UHTC materials.

Advances in Corrosion Science for Greater Safety, Reliability and Performance

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All of the infrastructure and systems needed to maintain our society are affected by corrosion. The determination of long-term performance of materials is crucial for safe and reliable systems, e.g. airplanes, bridges, pipelines, power plants and microelectronics. Significant contributions of scientific advances are illustrated for gas and oil, disposal of nuclear waste, automobiles, and medical devices.

The corrosion community has important opportunities and a responsibility to promote, develop and implement enhanced understanding. Preventive strategies to reduce corrosion costs were described in the NACE International study, *Corrosion Costs and Preventive Strategies in the United States.* A major finding was the need for further advances to performance assessment and life prediction. Progress is realized through increased scientific understanding, enhanced process models and advanced technologies for corrosion control.

Pitting-Induced Surface Alteration of Titanium

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The possibility to tune titanium surface morphology on the basis of the required application is fundamental in the use of functionalized titanium having particular surface properties, specially concerning the increase of titanium surface area [1-3]. Thus, on the basis of our previous works [4], principles of localized corrosion of passive metals in chloride containing environments were applied so as to develop a new surface modification treatment, which involved an anodizing step performed by supplying alternating current (AC) to titanium immersed in diluted HCl (anode-to-cathode potential difference: 5 V, frequency 50 Hz), aimed at modifying titanium roughness and preparing the surface for a second anodizing treatment (in direct current, DC), aimed at producing a photoactive oxide. The latter step requires the achievement of Anodic Spark Deposition (ASD) conditions, while the first step is straightforward, lasts only a few minutes and allows a good tuning of surface morphology by modulating the anodizing parameters.

Morphological changes actually consist of a pitting mechanism promoted by Cl⁻ and enhanced by AC on titanium surface, which causes the formation of a double texture of holes, being the surface of larger craters (tenths of μ m wide) studded with submicrometric holes. Moreover, the DC anodizing treatment itself confers to the surface a nanometric porosity, which combines with the AC-produced roughness. Oxides morphology was investigated by means of optical microscopy and SEM to evaluate the extent of pitted area, weight loss measurements to double-check pitting effects, and XRD to investigate the crystal structure of the oxide.

Alternative AC treatments were also tested, involving the use of HBr or HI; while the latter solution exhibited a much lower aggressiveness towards the metal, as expected, the HBr solution caused an extensive damage of the surface, which could not be only attributed to the pitting mechanism. In fact, the reason of this behaviour was ascribed to the presence of defective (and consequently electrochemically active) sites in the passive film of TiO₂, onto which Br⁻ chemisorption could occur and lead to the purely chemical dissolution of the passive layer.

To conclude, this anodizing procedure appears appealing as far as deep morphological modifications are desired in short process times, which reveals an interesting and useful exploitation of the localized corrosion phenomena.

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Quantifying Degradation Mechanisms of Alumina-Forming Alloys for Energy-Related Applications

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The renewed emphasis on energy-related materials research has focused efforts on providing critical information needed to implement new materials in these applications. Increased operating temperatures are needed to increase the efficiency of developing power generation technologies such as solar concentrators, combined heat and power turbine systems and fuel cells as well as conventional applications such as coal-fired boilers and gas-fired turbines. Challenges result from the extreme conditions under which the critical components are required to operate. Higher temperatures. particularly above 900°C, require alumina-forming alloys to meet the 25-100kh lifetime goals needed for reliable and economical power generation. However, there is a limited database of long-term performance for many alumina-forming alloys. A major issue is quantifying the rates of typical modes of degradation for these higher temperature applications as well as lesser-studied effects such as the decrease in mechanical properties during service. The main example will be oxide dispersion strengthened FeCrAl and Fe₃Al for use in heat exchangers and a methodology developed to predict time to breakaway as a function of wall thickness at 1100°C. Lifetime predictions are less reliable in more aggressive environments such as steam and CO₂-containing gases where the exposure database is limited.

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Development and Performance of Al-Rich Oxidation Resistant Coatings for Fe-Base Alloys

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Diffusion coatings to enrich the surface of conventional Fe- and Ni-base alloys have been studied for many years. The current study evaluated model coatings primarily made by chemical vapor deposition on ferritic (e.g. Fe-9Cr-1Mo) and austenitic (e.g. Type 304L) substrates to quantify potential benefits and to identify any problems with alumina-forming coatings. For oxidation testing, a humid air environment was used to identify coating failure during exposure, as uncoated substrates experience rapid oxidation in the presence of water vapor. Exposure temperatures of 650°-800°C were selected to accelerate the degradation of the coating by interdiffusion with the substrate. Cycle frequency and coating thickness were varied in order to demonstrate the effect of coating-substrate thermal expansion mismatch. The conclusion of this testing was that coatings with lower Al contents that remained in the ferritic Fe(Al) phase field could be more durable than higher Al content aluminide coatings.

Another goal of this project was to develop a lifetime model based on diffusion and oxidation data. A key parameter for the model is the coating failure criterion when the coating can no longer prevent the substrate from rapidly oxidizing. Coating failures at 700° and 800°C for a ~40 µm thick Fe(Al) coating on Fe-9Cr-1Mo showed very low critical Al contents, ~3.5at.% at 700°C and \leq 1at.% at 800°C. Similar thin coatings on 304L and 316 austenitic substrates have shown lifetimes >2X those on ferritic alloys without failure. The failure information was incorporated into the lifetime model to allow prediction of coating lifetime on ferritic alloys as a function of temperature and starting coating composition. A follow up study showed little effect of Cr content on coating lifetime at 800°C on ferritic alloys with 8-11 at.%Cr. Because of the unexpectedly low level of Al at coating failure, exposures of specimens with thick $(\sim 200 \mu m)$ coatings and higher Al contents were stopped after 10-20 kh at 700° and 800°C because extremely long times to failure were predicted. Post-exposure Al concentration profiles for these specimens were measured using electron microprobe and compared to model predictions. A significant decrease in Al interdiffusion for austenitic substrates was observed and this likely explains the observed longer coating lifetime for these alloys. However, a more sophisticated model will be required to predict coating lifetime on austenitic alloys.

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The polymer network structure as a key parameter for the corrosion resistance of polymer/oxide/metal interfaces

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Water borne latex dispersions are of increasing importance as primer layers on industrial relevant zinc and iron substrates. We investigated n-butvl acrylate (nBA)/styrene (Sty), 2-ethylhexyl acrylate (EHA)/Sty and nBA/EHA/Sty copolymer compositions with a glass transition temperature (T_g) between -40 °C and 40 °C. Electrochemical Impedance Spectroscopy (EIS) was applied to study the barrier properties of the latex layers towards water uptake and water diffusion through the polymer matrix. In-situ Scanning Kelvin Probe (SKP) measurements were used to determine the kinetics of cathodic delamination and ion transport processes along the polymer/oxide/metal interfaces. On the one hand it was detected that the progress of cathodic delamination characteristically increased with increasing glass transition temperature of the latex layers on iron substrates. No such correlation was observed when zinc was applied as substrate material. On the other hand it turned out that EIS was not a suited method to predict the stability of the polymer/substrate interface towards interfacial ion transport processes. A decrease of the average macromolecular mass at constant T_g resulted in a stabilisation of the interface. An increase of the polymer cross linking density at constant Tg led to a destabilization. For these modifications of the latices the water diffusion coefficient, determined by EIS, also changed significantly.

The presented experimental approach offers a further insight into the interaction of water diffusion through polymer matrices and of cathodic delamination on the resulting latex/ substrate interface stability. It will help to predict the ageing kinetics of adhesive joints in the future.

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Effect of Grain Size and Processing on the Corrosion Resistance of Aluminium

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Recent studies have shown that improvements in strength and wear resistance can be achieved through grain refinement. Although efforts have been presented in the literature, a complete understanding of how grain refinement, grain size, and processing affect the corrosion resistance of an alloy has not yet been developed. Determining a definitive 'grain size-corrosion resistance' relationship is inherently complex as the necessary processing to achieve refinement also imparts changes in microstructure (such as texture, internal stress, and impurity segregation), which may contribute or even dominate the electrochemical response. The objective of this work is to determine how variation in grain size and processing impact the corrosion resistance of high purity aluminium (99.999%). Aluminium samples with a range of grain sizes, from $\sim 100 \ \mu m$ to $\sim 2000 \ \mu m$, were produced using different processing routes, including surface mechanical attrition treatment (SMAT), equal channel angular pressing (ECAP), cold rolling and cryo rolling in conjunction with various heat treatments Electrochemical response was characterised primarily using potentiodynamic polarisation experiments in NaCl solutions. Corrosion current densities were not observed to depend on grain size (at least over the range studied here within). However, processing route had a significant effect on corrosion rate with the most corrosion resistant samples (ECAP) displaying corrosion rates nearly 2 orders of magnitude less than the most susceptible samples (SMAT). Additionally, passive current densities were observed to increase in magnitude as grain size decreased. Current and future work is focused on expanding analysis to other light alloys and commonly used commercial aluminium alloys.

The Role of Chromium in the Hot Corrosion of Metals

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The accelerated oxidation of metals and alloys by a thin surface film of fused salt is controlled by the local salt (acid-base) chemistry and oxidizing potential at the salt/scale interface, as can be monitored using ec surface probes. The solubility of chromium oxide in fused sodium sulfate as a function of melt chemistry at 1200K is accurately known, with chromate ions as the dominant solute at high oxygen activities, but chromite ions dominate at low oxygen activities. Since the chromia solubility increases with increasing oxygen activity, solid chromia is not expected to precipitate out in the salt film during hot corrosion.

Serving as a strong acid solute, formation of the chromate ion can serve as a buffer for the melt chemistry at the scale/salt interface. Chromite ions would react with the solutes of less acidic oxides, e.g. CoO, NiO, FeO, etc. to form chromate ions, thereby preventing the shift toward high local basicity, sulfide formation and oxide dissolution/reprecipitation. Furthermore, chromate ions can precipitate back onto reducing sites (scale grain boundaries and flaws) on the alloy surface to block its contact with the salt.

The Role of the Metal/Scale Interface in the Growth of Protective Scales on Metals

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A mechanistic methodology has been developed to understand the role of the metal/scale interface in the growth of scales at high temperatures. Specifically, cation vacancies arriving at the metal/scale interface are annihilated by the climb of misfit and misorientation interfacial dislocations. If this mechanism is blocked, e.g. by the tangling of dislocations within the metal, then cation diffusion cannot continue to support the growth of an adherent oxide. To the extent that adherent, crystalline and epitaxial passive or anodic films formed in aqueous environments also grow by cation diffusion over vacancies, the same mechanisms must apply.

The segregation of large reactive element cations to the metal/scale interface and their importance in enhancing scale adherence by blocking vacancy annihilation, also constitute concepts that might find relevance for passive films in aqueous solutions.

Engineered Coatings Using Pack Cementation Processes

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Metallic surfaces can be altered to achieve design objectives, e.g., corrosion resistance, wear or abrasion resistance, etc., using a wide range of coating methods. The particular method chosen is usually the result of the interplay of many factors including economics and design requirements. The focus of this talk will be on the development of coatings using Halide Activated Pack Cementation (HAPC). HAPC is a versatile and economical approach to apply coatings of desired compositions to a range of substrates, typically nickel and iron-based alloys. The coating process can be controlled to obtain the desired final composition and microstructure. The in situ generation of halide vapor species inside the pack with subsequent transport, surface reactions and solid state diffusion are important phenomena that need to be understood in order to achieve optimal coating conditions. In this talk, the halide-activated pack cementation process will be discussed in the context of the relevant thermodynamics and kinetics; the current status of our modeling and experimental work will be presented (Figure 1). Specific experimental examples, e.g., aluminide coatings on nickel (Figure 2), superhard coatings, etc., will be discussed.



Figure 1. Variation of rate constant with particle size for constant Al activity at the substrate (AlF₃-activated pack)



Figure 2. Optical micrographs showing aluminide coatings on Ni for coating times of 1,4,9 and 16 h at 700°C

Materials for High Temperature Thermal Shock Applications

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Platelet Reinforced Ceramic-matrix (PRC) composites prepared by the DIMOXTM Directed Metal Oxidation Process exhibit a unique range of microstructures, and attendant changes in fracture toughness. They have demonstrated excellent thermal shock performance in a range of rocket engine and motor tests. The $Zr-ZrB_2-ZrC$ system will be discussed along with Hf- analogues. Properties of the Zr-based system will be presented, along with test results from rocket engine and motor tests. Coatings based on titanium carbide will also be briefly discussed as potential short-term high temperature use materials.

Effects of Surface Treatments on Adhesion Strength of epoxy coated AA2024-T3 using the Blister Test

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Adhesion is one of the key parameters that affect the protective capability of the coatings. Nevertheless, there is a lack of knowledge about the enhancement of the adhesion strength of the substrate to the coating. The effect of surface topography and non-chromate conversion coatings in adhesion strength of epoxy and polyvinyl butyral (PVB) coated AA2024-T3 substrates was studied using the Blister Test with D.I. water and 0.5 M NaCl as pressurizing fluids. The adhesion strength is calculated by Linear Elastic Fracture Mechanics (LEFM) by means of the fracture energy from pressure, height and radius of the blister. It was found that epoxy primer provides very good adhesion; but it often fails cohesively before delaminating. Surface condition has a large influence on adhesion properties. Degrease and deoxidize treatment greatly improves adhesion over as-received condition. The coatings used experienced plastic deformation during the test making LEFM not valid. However, it gives an estimation of adhesion strength. Roughness increases adhesive strength of the PVB/AA2024-T3 interface. None of the samples treated with non-chromate conversion coatings showed delamination during constant pressure experiments at 1 bar in D.I. water and 0.5 M NaCl solutions.

Application of Conducting Polymers for the Corrosion Protection of Iron and Zinc

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Despite intense research on corrosion protection by conducting polymers over the last three decades, their technical application has not yet made its breakthrough. The reason for this is that most of the published work focuses on corrosion conditions where coatings based on conducting polymers do more or less work, while under more practical conditions they were found to fail, especially under atmospheric corrosion conditions. In our work we could successfully unravel the reasons for this discrepancy. These investigations were mostly based on well defined model samples that made it possible to separate different aspects of corrosion performance of conducting polymers.¹⁻⁶. Based on these findings clear guidance on how corrosion protection coating based on conducting polymers should look like in order to work properly can be given^{1,2, 4-5}.

In a nutshell, coatings composed only of conducting polymer are not suitable for general corrosion protection^{1,2}. More accurately, one prerequisite for positive performance is to avoid extended percolation networks of the conducting polymer in the coating, i.e. only composite coatings with not too high content of conducting polymer perform well, otherwise fast coating break down will occur²⁻⁵.

However, it had still to be shown that these guidelines will really work not only in model systems but also for protection of metals such as iron or zinc under more practical application conditions. First results will be presented.

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The Corrosion Behavior of Pure Copper in a Bentonite/Saline Groundwater Environment

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The principal strategy for high-level radioactive waste disposal in Sweden is to enclose the spent fuel in tightly sealed copper canisters that are embedded in bentonite clay about 500 m down in the Swedish bedrock. Besides rock movements, the biggest threat to the canister in the repository is corrosion.

'Nature' has proven that copper can last many million years under proper conditions, bentonite clay has existed for many million years, and the Fennoscandia bedrock shield is stable. The groundwater is saline, oxygen-free and reducing below a depth of 100-200 m. However, initially a limited amount of air will be left in the repository after emplacement.

The most important task from a corrosion perspective is to ascertain a proper near-field environment for the copper canister. The initial oxic period is considered the most harmful. With this in mind corrosion monitoring and electrochemical impedance spectroscopy have been applied to learn more about the behavior of pure copper in an oxic bentonite/saline groundwater environment. Wyoming bentonite sold under the commercial name MX-80 and groundwater from the Äspö Hard Rock Laboratory (containing about 180 mM Cl⁻) have been used.

Part of the copper electrodes in the bentonite test package have first been pre-exposed in the Äspö HRL since October 1999 up to retrieval from the HRL in January 2006, and others have been installed in the test package after retrieval. Exposure times in the bentonite test package are thus in the range 3-10 years. Corrosion potentials have been followed since 2006, the real-time corrosion monitoring was started already in 2001, and electrochemical impedance spectroscopy has been applied in 2006 and will be applied again early next year before terminating the test and start the post-test examination of the copper electrodes.

The measured corrosion potentials have proven stable and oxic conditions in the test package, the corrosion monitoring displays low but measurable corrosion rates, and the impedance measurements have been valuable both in adjusting the recorded corrosion rates from the real-time corrosion monitoring and in supplying information about the corrosion behavior of pure copper in the bentonite/saline groundwater environment.

Semiconductor Behavior of Passive Films Formed on AISI 316L Stainless Steel in Sulfuric Acid Solution

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In this study, the electrochemical behavior of passive films anodically formed on AISI 316L stainless steel in 0.05M H_2SO_4 solution have been examined using electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis. The passive range was determined to be from -0.2 to 0.8 V_{SCE} . Fig. 1 represents positive slopes up to 0.6 V_{SCE} , indicating n-type semiconductor behavior.



Fig. 2 displays that calculated donor density decreases exponentially with increasing film formation potential, indicating improvement in protective nature of the passive film. Fig. 3 shows a linear relationship between the steady-state film thickness (L_{SS}) and the formation potential. This increase of L_{SS} results in improvement in polarization resistance of the passive film up to 0.6 V_{SCE}. Whereas at higher potentials, oxidation of Cr³⁺ to Cr⁶⁺ decreases the polarization resistance, and the protective nature of the passive before entering transpassive region.



Formation of Crevice on the Surface of Simple and Timodified Aluminide Coatings under Molten Salt Deposit

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Hot corrosion phenomenon has been extensively studied in oxidizing conditions: however much less attention has been paid to the reducing conditions, which can be important in the microclimates encountered locally in practice. Simple aluminide coatings have the known vulnerability to hot corrosion in both environments. In this study, the hot corrosion behavior of simple and Ti-modified aluminide coatings on nickel-based superalloy B-1900 was investigated. Two different sodium sulfate salt deposition regimes were studied with the same salt loading parameter of 1 mg/cm^2 per 32 hours at 900 °C. Although the weight change data showed relatively more durability for the modified coatings, morphological observation of the specimens aided by the phase and elemental analysis revealed similar degradation mechanism for all coatings studied (Fig. 1). It seems that the bottom of pits developed at the oxide scale discontinuities are in the reducing conditions and can grow perpendicular to the surface into deep crevices. The growth and joining of these crevices let large pieces of the coating be lost and exposed the bare substrate to the molten salt at longer times. The way of initiation and advancement of the crevices is discussed and a model is proposed to explain this type of hot corrosion morphology.

Key words: aluminide coating, hot corrosion, Ti-modified, pit, crevice formation



Figure 1- Hot corroded simple aluminide coating. A crevice is observable under the detached part of the coating (arrow).

Repassivation Behavior of Ti in Artificial Saliva with PRM

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Titanium and its alloys show excellent medical compatibility, high strength, and very good corrosion resistance, therefore, it is commonly use in medical applications. These properties are related to the oxide films formed on titanium, however, the oxide film is sometimes removed or breaks down during use mechanically or chemically. To investigate the repassivation behavior is very important for the durability of titanium. One technique for investigating repassivation kinetics is PRM (the photon rupture methods where oxide film is removed by focused pulse of Nd-YAG laser beam irradiation). This technique enables area selective measurements for very short periods of repassivation without contamination from the film removing tools. The purpose of the present study is to investigate the effect of applied potentials and the concentration of F^- ions on the initial stage of the repassivation behavior of titanium in artificial salvia.

Titanium sheet (99.5 mass%, thickness 0.3 mm, Niraco Co.) cut into 10 x 20 mm² coupons was electro-polished in NaCl ethylene-glycol solution, and then anodized in 0.5 kmol m⁻³ H₃BO₃ / 0.05 kmol m⁻³ Na₂B₄O₇ solution up to 5 V at constant current density of 15 Am⁻². The anodized specimens were immersed in artificial saliva (pH = 4.8) with or without F⁻ ions, and then irradiated by one pulses of a focused laser beam at constant potentials. The current transients after the irradiation were measured.

Fig 1 shows the current transients after laser beam irradiation at different potentials in F⁻ ion free artificial salvia. By laser irradiation. the current increases instantaneously through a maximum at about 2 ms, and then decreases exponentially with time at every applied potential. The current and peak current increase with increasing applied potential. These results suggest that localized dissolution before the peak current is enhanced by the applied potential. However the current decreases after the peak, meaning that the oxide film is formed at laser bean irradiated area. The slopes of the log i vs. log t curves after 10 ms are steeper than -1. This suggests that the film formation kinetics do not follow an inverse logarithmic law.



Fig. 1 Current transients after laser beam irradiation at different potentials in artificial salvia.

SEM/EDS and SKPFM Study of Chromium Nitrides in Duplex Stainless Steels - Limitations and Implications

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Chromium nitrides precipitated in stainless steels may have a detrimental effect on both mechanical properties and corrosion behaviour ¹. In duplex (ferritic-austenitic) stainless steels chromium nitride precipitates can be formed in the ferrite phase after fast cooling from the solution annealing temperature of 1050°C or at the ferrite/austenite boundaries after isothermal heat treatment at approximately 800°C. SEM/EDS and scanning Kelvin probe force microscopy (SKFPM) techniques have been used to study heat treated superduplex 2507 stainless steels with both isothermal and quenched-in chromium nitrides, in addition to the ferrite and austenite matrix. The SEM/EDS was performed to obtain the compositional contrast and elemental composition of the phases and the SKPFM to give the Volta potential variation of each phase. The measurements were carried out on the same surface area to enable the direct comparison between the results from two techniques. The phases in the Volta potential map can be easily recognized using BSE-SEM micrograph.

The isothermal chromium nitrides exhibit a higher Volta potential than austenite and ferrite, respectively, which reflects their higher nobility. This is primarily attributable to the higher Cr and N contents. The adverse effect of the isothermal chromium nitrides can be explained by the local Volta potential drop at the ferrite/austenite boundaries as a result of the local elemental depletion, particularly Cr and N. Moreover, the size effect on the measured Volta potential can be observed. The small chromium nitride particles showed lower Volta potential than the larger ones due to the influence of the surrounding matrix. The quenched-in chromium nitrides showed no contrast in Volta potential map. This could be because the size of these nitrides is smaller than the lateral resolution of SKPFM technique², crystallographic effect may also make a contribution. The absence of the quenched-in chromium nitrides in the Volta potential image indicates that they have no detrimental effect on the corrosion resistance in this material. This is in general agreement with industrial experiences for this material.

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Application of Inkjet Printing for Salt Deposition Prior to Atmospheric Corrosion Testing

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This study examined the feasibility of using piezoelectric inkjet printing for quick, precise and controlled deposition of soluble salt particles on metal samples for atmospheric corrosion testing. A commercial off-the-shelf consumer inkjet printer that could handle planar samples up to 12 cm x 12 cm was utilized for this purpose. Patterns comprised of line, dot and rectangular elements of varying sizes were constructed in vector drawing software and printed to determine the capabilities of the printer in reproducing small pattern elements without distortion. The amount of salt the printer could deposit along with the precision of the deposition amount was examined by printing either an array of 150 μ m wide lines or a 1 cm² solid square pattern using 1M and 4M aqueous NaCl solutions for each pattern. A total of 120 prints, 30 for each combination of solution concentration paired with print pattern, were laid out on an equal number of inert plastic coupons. Each coupon was rinsed after printing and the conductivity of the rinse measured to determine the amount of deposited salt. The same print patterns were also laid down on metal surfaces and examined using optical microscopy and image analysis software to determine particle size and distribution over the printed surface. The results indicate that the printer used for this study was able produce line elements and rectangles down to approximately 150 µm wide and circles to a diameter of 700 µm without general distortion. The deposition density of the 1M and 4M NaCl squares averaged $79\pm1 \text{ µg} \cdot \text{cm}^{-2}$ and $177\pm2 \text{ µg} \cdot \text{cm}^{-2}$ respectively at 95% confidence. Similar deviation was found for the line pattern prints. Deposition density could be tuned by modifying the print pattern or by repeated printing over the same area, resulting in a range of less than 1 μ g cm⁻² to over 1 mg cm⁻². Particle size and distribution was found to be dependent on the print pattern and the hyrophobicity of the printed substrate. This study has shown that piezoelectric inkjet printing using an offthe-shelf printer can provide the highly precise and uniform chemical deposition necessary for atmospheric corrosion testing.

Development of an Electrochemical Method of Detection of Sensitization in Al-Mg Alloys

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As part of a program to develop a non-destructive, electrochemical method for the detection of degree of sensitization (DoS) in 5XXX series aluminum alloys, a study was performed to optimize the solution used in that testing. The experimental procedure for measuring the DoS consists of exposing the AA5456-H116 to a pH 11 commercially certified phosphate buffer solution and conducting a thirty-minute opencircuit potential (OCP) measurement, followed by a thirty-minute potentiostatic hold, and concluding with a fifteen-minute OCP measurement. The time course of the final OCP measurement has been shown to reflect the DoS level of the AA5456 material, as determined by ASTM G-67 testing. During the development of the testing, it was found that there was some variability in both the measured pH of the buffer solutions and the response of the alloys to those solutions. This study investigated the roles that pH and buffer phosphate concentration have on the ability to differentiate between DoS levels based on electrochemical parameters extracted from the procedure. To better understand these dependencies, the electrochemical behavior of beta and AA1100 were also studied From these experiments and Pourbaix diagrams, kinetic and thermodynamic information was extracted and used in the optimization of the buffer solution composition for DoS testing.

Failure and Reliability Issues of Equipment in a Large Natural Gas Liquids Processing Plant

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Hess is the operator of the Seminole Gas Processing Plant (SGPP) in West Texas, which was originally commissioned in December 1984. SGPP expanded its initial capacity from 160 mmscfd to 270 mmscfd today. The plant processes gas produced from the adjacent oilfield with an inlet stream of 90% CO2. The CO2 is recycled back to the field as part of a tertiary oil recovery project. The remaining natural gas is processed via three refrigeration compressors and the natural gas liquids (NGL) product is stored in seven carbon steel NGL pressure vessels.

There have been two major plant integrity issues: a catastrophic failure of a first stage power turbine disk upstream of a refrigeration compressor in September 2008; and the discovery of HIC and SOHIC in multiple NGL pressure vessels in 2009. Several of these vessels were being used to recycle off spec sour product during upset periods.

The failure of an A-286 turbine disk resulted in a multi-million dollar repair. An extensive study was conducted to determine the failure mechanism. Creep calculations based on temperatures predicted from thermal models showed creep life exceeding 100 years. Sustained and cyclic stresses calculated by the stress model are well below the fatigue S-N curve for A-286 at 1000F. The fracture initiation site showed the presence of primarily intergranular cracking with oxide filled grain boundaries and numerous secondary intergranular cracks.

The study findings pointed to the mechanism described by Woodford¹ as gas phase embrittlement, which is related to oxide formation at the crack tip. For nickel based alloys in high temperature air there exists a temperature dependent minimum in ductility and a corresponding maximum in crack propagation rate. The crack likely propagated at loads lower than predicted by creep rupture or mechanical fatigue alone. Hot ductility tests are ongoing with samples of the failed turbine disk (102,000 hours service). Dwell fatigue tests at high temperature at very low frequencies are planned.

A rigorous risk based inspection project in 2009 identified the potential for HIC/SOHIC in the NGL vessels. Subsequent inspections were carried out using API 580 and 581. More rigorous fitness for service calculations per API 579 were used to condemn several of the vessels, preventing a potentially catastrophic failure.

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Moisture-Induced Alumina Scale Spallation: The Hydrogen Factor

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The performance of advanced turbine engine airfoils depends on the growth and adhesion of protective alumina scales on single crystal Ni-base superalloys and their bond coatings for thermal barrier coatings (TBC). For some time our community has been concerned with interfacial spallation of protective alumina scales, occurring primarily upon immediate cooldown, but also as a time-delayed phenomenon. The terms moistureinduced delayed spallation (MIDS) and desktop spallation (DTS) of TBC's have been coined to refer to the latter process. It becomes most apparent for relatively adherent alumina scales that have survived cool down in a dry environment, built up considerable thickness and strain energy, and have been somewhat damaged, such as by cyclic oxidation cracking. Indeed, a "sweet zone" can be defined that maximizes the observed effect as a function of all the relevant factors. Moisture has been postulated to serve as a source of interfacial hydrogen embrittlement, derived from reaction with aluminum in the alloy at an exposed interface. The purpose of this monograph is to trace the close analogy of this phenomenon to other hydrogen effects, such as embrittlement of bulk aluminides and blistering of alloys and anodic alumina films. A formalized, top-down, logic tree structure is presented as a guide to this discussion, starting with demonstrations of hydrogen as a reaction product between Al and H_2O . This is followed by a first principles theoretical prediction of interfacial weakening by and detection of interfacial hydrogen. Further support is provided by critical experiments that produce effects similar to moisture, but with hydrogen isolated as the causative factor. These experiments include tests in H₂-containing atmospheres or cathodic hydrogen charging, as shown below:



Passivity, Breakdown and Etching Rates of Silicon in Alkaline Solutions

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Electrochemical etching is one of the most effective and inexpensive techniques for fabrication of three-dimensional structures, which offers several advantages over other etching techniques, such as, wide variations in etch rate, accurate control and monitoring of the etching processing.

Traditional electrochemical etching is usually associated with anodic polarization within the potential range of active dissolution. The wider this potential range is, the higher the etching rate. Considering silicon, a wide potential range of active anodic dissolution occurs only in solutions containing hydrofluoric acid (HF) [1]. It is thought that in HF-free aqueous solutions, silicon is either totally passive, or active only in a narrow potential range, as in the case of alkaline solutions [1], with inability to regulate the etching rate. However, it was established in our previous studies that a high dissolution rate (above 4μ m/min) of silicon can be achieved in alkaline solutions under application of negative (cathodic) potentials [2].

Here, we demonstrate the possibility of p-Si etching in alkaline solutions by applying positive (anodic) potentials. The attempt to accelerate silicon etching using anodic polarization doomed to fail at first glance, since in HF-free solutions silicon undergoes anodization in a wide potential range. In many acidic and neutral aqueous solutions silicon anodization occurs up to voltages above 100 V [1]. However, in alkaline solutions, the range of silicon anodization is much lower (less than 20 V)[1].

In order to clarify anodic behavior of p-Si in alkaline solutions, potentiostatic measurements in a wide potential range between OCP and +60 V were performed. We show that the etch-rate of p- silicon strongly increases with potential in potential range above 20 V. The most significant acceleration in etch rate was obtained between 30 and 40 V. A maximum etch rate of 32 μ m/min was achieved in 50 wt% KOH solution.

The effect of applied potential, solution concentration, and other parameters on electrochemical behavior of p-Si, its dissolution rate and topography of etched Si surface will be discussed. Features of silicon dissolution under negative and positive applied voltages will be compared.

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Influence of the Nano Oxide Metal Films on the Interaction with Organic Coatings

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The adhesion and delamination of organic coatings is mostly determined by the oxide film between metallic substrate and polymer film. The aim of this study is to examine the effect of the interfacial oxide on the adhesion and delamination rate of organic coatings. To do so, the oxide surfaces on different metals (Al, Zn, Fe) were characterized first by means of XPS, FTIR, Contact Angle measurements and Electrochemical Impedance Spectroscopy (EIS). The hydroxyl fraction, surface energy and semiconductor properties could be determined. Next, the surfaces were contacted with monomers having different functionalities (carboxylic acids, silanes, amine and amide) to determine the affinity of the differently prepared oxides towards bonding. The next step was to characterize the interaction with the monomers by Kelvin probe potential measurements. The last part discusses the coating delamination.

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A Coating Combination of Self-healing Polymers and Corrosion Inhibitors for Active Corrosion Protection of Metals

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A polyurethane (PU) based segmented block copolymer with polyester (PCL) soft blocks was deposited as a coating. This physically crosslinked polymer system shows a self-healing ability based on the fracture and reformation of thermally reversible physical bonds in the polymer matrix. Because heat is necessary to trigger and assist the healing process, these materials are classified as non-autonomic healing polymers. The investigated polymer system is generally not used for coating of metals, hence its potential as a coating material was explored. Additionally cerium nitrate was added to the coating formulation as corrosion inhibitor. As such a multiple action self-healing coating system was created based, on the one hand, on the inhibitor passivating the metal when the coating is damaged and the metal exposed to a corrosive environment, and on the other hand, on the ability of the coating material itself to physically heal a sustained local damage resulting in the repair of the barrier properties. The healing ability of this combined polymer system was studied in bulk and as a coating using various thermomechanical analyses and Electrochemical Impedance Spectroscopy (EIS). First results indicate that when the coatings are locally damaged by scratching, a thermal treatment to a temperature above the melting point of the soft PCL phase in the block copolymer and below the melting point of the hard PU phase, results in coating repair as observed using AFM and in a regaining of its barrier properties as observed with EIS.

Smart Functionalized Polymer Dispersions for Effective Mapping of Heterogeneous Metal Surfaces: New Concepts for Corrosion Protection

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The development of environmental friendly coatings for corrosion protection of steel continues to attract a great deal of attention. Within this paper we present a new concept for corrosion protection based on functionalised water borne latexes and their application to heterogeneous metal surfaces such as hot dip galvanized (HDG) steel.

It is well known that industrial HDG steel samples show a heterogeneous surface. In the first part of this paper we characterised the different surface chemistry and their susceptibility for the corrosion process. The characterisation of the surface was performed with a high lateral resolution on a nanometre scale by Scanning Auger Microscopy (SAM) and Energy Dispersive X-Ray Spectroscopy (EDX) attached to an ultra high resolution Field Emission Scanning Electron Microscopy (FESEM). The electrochemical mapping was obtained by a micro Scanning Capillary Cell (SCC) and Scanning Kelvin Probe – Force Microscopy (SKP-FM).

In the work for the second part of this paper, we synthesized water borne polymer dispersions with different functional anchoring groups on the surface of the dispersion particles and investigated the adsorption of these latexes to the HDG steel surface during a dip coating process. It was possible to design polymer particles, able to map the heterogeneous substrate surface effectively.

The combined micro-electrochemical investigations and the synthetic approach, designing latexes for very selective surface adaptation, could provide a new route to "smart coatings" adapted to the very specific heterogeneous chemical and electrochemical properties of industrial steel surfaces.

High-Temperature Sulfidation of Alumina-Forming Alloys

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High-temperature sulfidation resistance is a critical materials need for powergeneration and propulsion applications in sulfur-bearing environments. This paper discusses high-temperature reaction mechanisms and associated sulfidation resistance of alloys with a focus on those that form alumina. Results for Fe-Al-Cr and Ti-Al-Cr systems indicated that good sulfidation resistance can be achieved when environmental and alloy conditions promote (almost) exclusive formation of alumina. The differences in the "third-element" effect associated with Cr in the respective alloy systems under high sulfidizing/low oxidizing potentials are discussed.

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Turning Corrosion Around: Using High-Temperature Oxidation Principles for Synthesis of Functional Materials and Application to PEM Fuel Cell Bipolar Plates

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This paper describes how principles of high-temperature oxidation of alloys can be used as an approach for controlled synthesis. Alloy microstructural and compositional modifications can be used to tune high-temperature environmental reactions to achieve desired near-surface structures/products. Multi-phase alloys present particularly interesting opportunities as they can act as microstructural templates for synthesis of unique composite structures under certain conditions. Simple, specific examples of using selective oxidation (nitridation) principles to form electrically conductive, corrosion-resistant surface layers on nickel- and iron-based alloys for application as bipolar (connector) plates in proton-exchange-membrane fuel cells will be described.

Research sponsored by the U.S. Department of Energy: Fossil Energy Advanced Research Materials Program, Office of Fossil Energy and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Fuel Cell Technology.

The effect of cold work due to shot peening on the steam oxidation resistance of Type 304H austenitic stainless steel

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Coal-fired power plants provide nearly half of the electricity to the power grid in the United States. Plant maintenance outages are often planned events that have a known financial impact on a utility company. Unexpected plant outages and have been experienced due to excessive steam-side oxidation of superheater tubes and subsequent exfoliation of iron-based oxides. The internal scales formed on these tubes are composed of at least two different types of oxide. The scale that forms immediately adjacent to the fluid is primarily magnetite. The inner oxide adjacent to the base metal

adjacent to the fluid is primarily magnetite. The inner oxide adjacent to the base metal is an alloy spinel oxide. During cool down of the unit for an outage, the difference in thermal expansion of the outer scale and the base metal causes the magnetite to spall.

Exfoliated scale collects in lower tube bends, creates blockages, and inhibits steam flow. The blockages may go undetected until unexpected failures occur due to overheating in the downstream tubing.

Investigators report an improvement in oxidation and exfoliation resistance in coldworked austenitic stainless steel exposed to steam. Most of the available literature discusses laboratory-produced ingots with controlled chemistry, grain size, and degree of cold work. The supporting theory describes a mechanism by which chromium diffusion is improved by increasing the grain boundary density at the free surface. The current work compares the rate of steam-side oxidation on Type 304H stainless steel (304H) tube after shot peening the internal surface with commercially available techniques. Three shot sizes (0.020", 0.035", and 0.25") and two peening techniques were examined. An untreated section of 304H was used as a control sample.

The samples were characterized in the as-treated condition prior to steam exposure using the following techniques; residual stress depth by x-ray diffraction, Knoop and Vickers micro hardness profiles, grain size, chemical analysis by energy dispersive spectroscopy, and microscopic documentation using an inverted light metallograph and a scanning electron microscope. The samples were exposed to superheated steam at 1150°F under 1 atmosphere of pressure for 1000 hours and 5000 hours. This paper compares the oxidation resistance by presenting the microscopy results, scale thickness measurements, and chromium distribution following each exposure interval.

AC Corrosion Mechanism on Buried Pipelines

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Buried pipelines for gas or petroleum transportation are generally protected against the corrosion by a thick organic coating completed by cathodic protection (CP). This system generally protects the pipelines satisfactorily. However, when the pipelines are located along with a high voltage current source, such as a high voltage power supply or railways, the corrosion of pipelines are sometimes observed. Mechanisms of AC corrosion of pipelines under CP, and CP criteria for its mitigating remain subject of controversy. AC corrosion behavior of carbon steel was examined by Raman spectroscopy, simultaneous recording of potential and current, and by direct corrosion feature, of some critical parameters namely AC current density, AC voltage amplitude, CP level, soil resistance between the coating defect and remote earth, and development of iron oxide layers.

In Situ Corrosion Monitoring of Ti-6Al-4V Alloy in H₂SO₄/HCl Mixed Solution Using ECAFM

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Electrochemical atomic force microscope (ECAFM) was employed for in-situ observation of corrosion occurred on Ti-6Al-4V titanium alloy in 0.5 M H₂SO₄ + 1 M HCl mixed solution. A scanning electron microscope (SEM) with the energy dispersive spectroscope (EDS) attached was also used for surface morphology and chemical composition analyses. The chemical composition difference between the air-formed oxide presented on α and β phases was analyzed by conducting Auger electron spectroscopy (AES) concentration depth profile. For solution annealed followed by furnace-cooled Ti-6Al-4V titanium alloy, the dissolution of passive film and the selective corrosion of α phase could be clearly observed under ECAFM. The experimental results showed that the air-formed oxide films on α and β phases had different stabilities in 0.5 M H₂SO₄ + 1 M HCl mixed solution. The film present on α phase would dissolve preferentially as compared with that on β phase. A higher dissolution rate was also found in α phase than β phase on the bare Ti-6Al-4V titanium alloy. Galvanic effect was also observed at α / β interface, causing non-uniform corrosion in β phase.



Fig.1. AFM images showing the progress of corrosion process of the furnace-cooled Ti-6Al-4V alloy (a) initial condition (as-polished), and after immersion in 0.5 M $H_2SO_4 + 1$ M HCl mixed solution under open-circuit condition for (b) 80, (c) 140, and (d) 200 min, respectively.
A Novel Method to Measure In-situ Corrosion and Degradation Reactions Occurring inside Pressurized Aerosol Containers

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Over three billions aerosol containers are produced in the United States annually. Manufactures of pressurized aerosol containers conduct exhaustive (and time consuming) corrosion screenings for each formula and its variations prior to releasing the product to the general public to minimize failures.

Electrochemical attack of the aerosol pressurized containers (i.e., corrosion) is one of the primary failure modes and can result in pitting and crevice corrosion, that can lead to perforations, and general corrosion, which has the potential of altering the product. The root cause for the failures can vary from the interaction between the formula and the non-lined container, failure in the lining and further attack by the formula and diffusion of the aggressive species through the lining and subsequent corrosion of the underlying container. Currently, most corrosion evaluations require a six to nine months static storage testing (SST) at room temperatures and elevated temperatures.

Typically, formulation screenings will include electrochemical approaches such as open circuit potential (OCP) monitoring, cyclic potentiodynamic polarization (CPP), linear polarization resistance (LPR) and/or electrochemical impedance spectroscopy (EIS). Unfortunately, these electrochemical approaches are only evaluated at ambient conditions and ambient pressures and do not accurately reflect the real environment within the finish product.

In this paper, a novel approach for conducting in-situ electrochemical measurements (i.e., OCP, CPP, LPR and EIS) within a fully pressurized aerosol canister will be discussed. In addition, the merits for coupling of an in-situ electrochemical evaluation with long term SST will be explored, mainly with respect to various formulations and substrate materials (i.e., steel and aluminum containers).

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The Oxidation Behavior of Commercial Alumina-Forming Austenitic Steel

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There have been numerous attempts over the past 30 years to develop an aluminaforming austentic steel with good creep properties and excellent high temperature oxidation resistance due to the formation of a highly-stable alumina external oxide scale. By optimizing the Al, Cr, Ni and Nb contents, a new class of steel has been developed that is fully austenitic with creep strength equivalent to the best austenitic steels. However, the relatively low Al and Cr contents appear to limit the maximum application temperature to ~900°C. At higher temperatures, the alloy is unable to form alumina or breakaway oxidation has been observed at relatively short times, particularly in the presence of water vapor. Oxidation results at 650°-800°C show promising performance for AFA steels suggesting a variety of applications including thin-walled heat exchangers for recuperated gas turbines and fuel cells. Commercially cast heats have been made of several promising compositions and current data is presented on the performance of sheet and foil (~100µm thick) specimens in air, humid air (to simulate exhaust gas) and steam.

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Environmental humidity influence on a topcoat/Mg-rich primer system with embedded electrodes

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Real time monitoring of Mg-rich primers beneath Air Force topcoats would provide a predictive means for the protection offered to the AA 2024-T3 substrate if a correlation can be obtained between monitored parameters and actual performance. A system comprising of a polyurethane topcoat with an epoxy primer pigmented with Mg particles was outfitted with six embedded electrodes on a 60 cm by 30 cm AA 2024-T3 substrate. The system was placed in a glove box and exposed to humidity levels ranging from 40 % to 90 % with the temperature fixed at 30 °C. Electrochemical impedance spectroscopic (EIS) experiments were performed between the electrodes and the substrate and between pairs of electrodes using a two electrode configuration. Electrochemical noise method (ENM) experiments were conducted using pairs of embedded electrodes and the substrate in a non-conventional reversed, single substrate configuration. The data was analyzed to provide the influence that environmental humidity had on the performance of the Mg-rich primer. The EIS data provided barrier and dielectric changes while the potential and current noise responses of the ENM data was statistically analyzed. The cathodic protection of the Mg-rich primer through the open circuit potential (E_{OC}) was monitored periodically by immersion of two 7 cm² areas of the coated substrate. Correlation between E_{OC} performance and the EIS and ENM parameters provided details on the applicability of coupling electrochemical measurement and embedded electrodes for monitoring systems with Mg-rich primers.

Modeling the fast initial stages of copper corrosion using multisine EIS combined with supporting experimental techniques

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Copper is still one of the materials used most by man. In many of the existing applications, corrosion still causes major problems and challenges. As a result copper corrosion in chloride containing media was already studied extensively, but still some unclarities remain. Especially the first hours of immersion remain a challenging domain because the surface undergoes multiple changes in this stage [1]. To gather information in this stage, multisine electrochemical impedance spectroscopy (EIS) was used [2].

A certain amount of the corrosion studies available in literature employs EIS to reveal the mechanism and parameters involved in this corrosion process. This type of experiments usually results in the proposal of an equivalent circuit or a mathematical model. The parameters herein represent the different parts involved in the mechanism of the corrosion. Among these models, some suffer from mutual contradictions [1].

It was observed that in solutions with a chloride content of about 0.5 M, the copper surface is attacked both by local corrosion at the grain boundaries as well as general corrosion at the surface of the grains. Using the multisine EIS technique, the evolution of the impedance response of copper electrodes in chloride containing solutions was investigated. As experimental parameters, the chloride concentration was varied around 0.5 M and various immersion times were studied. EIS results were complemented by gathering additional experimental data using Auger spectroscopy, Raman spectroscopy and SEM. As a result it was possible to identify by deduction the origin of certain relaxations present in the EIS spectra.

This procedure led to the proposal of a new model, being capable of describing more adequately the state of the copper surface in chloride containing solutions in the initial hours of immersion.

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Passive properties of duplex stainless steels after long-time ageing in air studied using EBSD, local electrochemical impedance spectroscopy, XPS and Auger

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Duplex stainless steels are highly important engineering materials, due to their generally high corrosion resistance combined with high strength and moderate alloy cost (lower nickel and molybdenum content). They are widely used in various industrial sectors, such as oil & gas (pipelines and storage tanks), desalination (evaporators and pumps), pulp and paper (digester and bleaching reactors) industries.

Duplex stainless steels have a complex microstructure with comparable volume of austenite and ferrite. Due to differences in chemical composition and mechanical properties between austenite and ferrite, a heterogeneous passive film may be formed on both phases.

In the present paper, changes in the chemical composition of passive films and the electrochemical behavior of UNS S32304 were analyzed at the micro-scale considering metallurgical and mechanical parameters. Effect of long-time ageing (in ambient air for 1 year, at 25°C) on passive properties was also analyzed by means of surface analysis methods (XPS, Auger) and local impedance spectroscopy based on the use of capillaries. The former experiments were carried out after 25 min immersion at OCP in 1M NaCl at 25°C (steady state) using 50 µm in diameter capillaries. The frequency range considered was 100 kHz-1 mHz.

Grain orientation was mapped using electron backscattering diffraction (EBSD) technique whereas the chemical composition of metallic phases was quantified by means of Castaing's probe. Residual stress field induced by surface preparation was calculated adopting finite element method.

After long-time ageing, grain orientation has small effect on the passive properties of ferrite. Two time constants were systematically identified in impedance diagrams (oxide film and interface represented by two R/CPE connected in series). By contrast, residual stress has strong influence on the shape of impedance diagrams and XPS/Auger profiles. Austenite generally behaves as a blocking electrode (represented by a resistance in series with a CPE). However, some grains with well defined crystallographic orientation were found to behave nearly like ferrite (two time constants). Residual stress has small influence on the shape of impedance diagrams and XPS/Auger profiles.

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Experimental Evidence of the Inhibition of the Oxygen Reduction on Galvanized Steel Cut-edges

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After immersion in dilute NaCl solution of a HDG galvanized low alloy carbon steel sheet (obtained from Arcelor), precipitation of mainly zinc dihydroxides occurs and forms a line of white precipitates on the steel. As shown in Fig.1, this line is almost parallel to the cut-edge length and split in two parts the steel electrode: (i) a zone beyond the line where zinc based white precipitates are observed (zone I) and (ii) a zone close to the coating where almost no corrosion products are visible (zone II).



Fig. 1. In-situ image of the surface of the sample HDG after 27 min (a) or 5 h (b) of immersion in 0.03M NaCl solution.

Complementary ex situ and in situ local probes techniques: Scanning Auger Electron Microscopy, Scanning Vibrating Electrode Technique (SVET), Scanning pH probe, Micro Electrochemical Capillary cell, were combined to elucidate the chemical processes at the origin of the formation of the inhibited zone II.

On the basis of these local analysis, this inhibition was found to be due to the formation of a zinc based hydroxide film by heterogeneous nucleation at the steel surface, which process was controlled by an increase of the interfacial pH.

These experimental results were validated by a numerical model developed to fit current density profiles measured by SVET. This model was discussed to propose a mechanism for the cut-edge corrosion of immersed galvanized steels.

Study of Crevice Corrosion by Coupling pH Measurements by TIRFM with FEM Modeling

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Recent literature indicates that the complexity of the models presented in the field of corrosion in occluded zones, like crevice corrosion, increases faster than the development of original experimental techniques allowing their validation. However increasing the complexity of a model accounting for electrochemical and chemical reactions with transport across an occluded environment like a crevice is meaningless in absence of experimental validation. This is the reason why we developed an experimental approach allowing to map the pH distribution in rigorously controlled occluded areas, in order to stick, as far as possible, to the geometries reported in simulations.

Micro-Cavities were patterned using photolithography on various substrates (steel and stainless steel). pH distribution in occluded conditions under anodic polarization were measured in these cavities using Total Internal Reflexion Fluorescence Microscopy (TIRFM) presented in Figure 1.



Fig. 1- Schematic description of the pH probe (a) and top-view of a 304L cavity after anodic polarization (b).

In our experimental conditions, initiation of crevice corrosion on 304L resulted systematically from a local activation inside the crevice (Fig. 1), related most probably with metallurgical factors (presence of MnS inclusions).

A simple 1-D mass transport model was proposed, allowing to simulate the evolution of the pH inside the crevice.

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Chloride-Induced Filiform Corrosion of Magnesium

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There is currently some confusion in the scientific literature regarding the nature of filiform corrosion (FFC) affecting magnesium substrates. Over the past fifteen years or so, reports of FFC occurrence on magnesium and its alloys result from experiments conducted under immersion in bulk chloride-containing electrolyte. However, FFC is more commonly recognized as an atmospheric corrosion phenomenon affecting organic coated metal surfaces, and is treated as such in research reports which pre-date the past two decades. In this work we demonstrate using commercial purity magnesium that FFC can be observed on the same substrate under both immersion and atmospheric corrosion conditions in the absence and presence of an organic coating respectively.

An in-situ scanning vibrating electrode technique (SVET) is employed to map localized corrosion currents occurring on unpolarised magnesium showing filiform-like features in 0.01 mol dm⁻³ aqueous sodium chloride solution. Immersion FFC consists of populations of dark threads of width 0.01–0.03 mm, which lengthen with time at a rate of 10^{-3} mm s⁻¹ and evolve hydrogen. The leading edges of filament populations are shown to be local anodes with measured local current densities of between 5 and 15 A m⁻², while the remainder of the corroded surface is a net local cathode and the intact, uncorroded surface is electrochemically inert. The same behaviour is observed when an identical experiment is carried out in a de-aerated electrolyte. These findings suggest that immersion FFC involves significant galvanic coupling of cathodically-activated, corroded regions with anodic attack at the interface with the intact magnesium surface and is not a form of localized corrosion caused by differential aeration. Consequently it appears unlikely that the mechanism of immersion FFC comprises propagation beneath an intact oxide layer, as has been suggested elsewhere.

Using the same substrate, it will also be demonstrated that FFC is observed beneath a model organic coating under atmospheric corrosion conditions. A combination of insitu scanning Kelvin probe (SKP) potentiometry and time-lapse photography is used to study the kinetics of underfilm corrosion under conditions of high relative humidity. Following initiation by aqueous hydrochloric acid (HCl), underfilm corrosion is characterized by the onset of coalesced filiform-like features, which lengthen with time and propagate at a rate which is largely independent of the quantity of initiating HCl. The potentials of the advancing underfilm corrosion-front range from -1.35 to -1.45V vs SHE, with corrosion potentials in the tail region largely similar to those of the intact coated Mg surface. The rate of corrosion filament advance is shown to be insensitive to the presence of oxygen, while chloride ion activity is maintained at the head of the underfilm corrosion front. The mechanism of propagation is proposed to involve anodic Mg dissolution at the leading edge of the corrosion front, galvanically coupling with hydrogen evolution on a cathodically activated corroded region behind.

Development of an Electrochemical Quartz Crystal Microbalance Probe for Corrosion Testing in Flow Loops

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Corrosion is an electrochemical process that can be monitored by various techniques, such as linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and electrochemical noise (ECN). The parameters that are measured by these techniques are governed by changes that occur on sample surfaces, such as metal loss due to corrosion, inhibitor absorption or corrosion product formation. The electrochemical quartz crystal microbalance (EQCM) can monitor the in situ mass change on the quartz crystal surface simultaneously with electrochemical measurement. This makes it a valuable tool in corrosion studies. However, it is difficult to apply the EQCM under realistic and well characterized flow conditions with commercially available probes. A new EOCM probe has been designed to be tested for application in flow loops. This has been tested at 25°C, 80°C and during ramping between these temperatures. The signal obtained from the new EQCM probe was compared with the conventional probe. There was good agreement between both probe types. The resonance frequency of quartz crystal changes and stabilizes under different flow rates when the flow is stable. The accuracy of measurement with the new probe was proven by applying a galvanostatic current through an iron coated quartz crystal. The mass change rate measured by the EOCM probe matched well with the applied current. It was proven that the new EQCM probe works properly and will be a great benefit for corrosion studies.

Corrosion Monitoring with CNT-Enhanced Fiber Sensors

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Carbon nanotubes (CNTs) are intensively studied due to their high electrical and thermal conductivity, strength, stiffness, and toughness.^{1, 2} CNTs also enhance the electrochemical reactivity and electron-transfer reactions not only in inorganic materials but also organic materials.³ CNT-enhanced fibers and tows therefore are of interest as in situ sensors in composite materials and fiber-metal laminate materials.

In this study, CNTs were grown on carbon and glass fibers using the chemical vapor deposition technique. The conductivity of CNT-coated carbon and glass fibers were determined by measuring the CNT interaction with the carbon and glass fibers in 3.5 wt% NaCl solution. In addition, the CNT-coated carbon fibers were electrochemically coated in 0.1 M Al(NO₃)₃.9H₂O solution. Sputter deposition was used for the coatings of both pure Al and Al alloys on both glass and carbon Fuzzy fibers. These CNT-enhanced fibers were immersed into a solution of 3.5 wt% NaCl to study their corrosion behavior. Figure 1 shows the corrosion potential behaviors of the CNT-coated fibers in 3.5 wt% NaCl. Detailed results will be presented.

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Figure 1. Corrosion potential behaviors of the CNT-enhanced fibers in 3.5 wt% NaCl.

Structure and Composition of an Alloy 22 Surface Preoxidized at Different Conditions.

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Ni-based alloys are highly corrosion resistant materials owing to an adherent and highly insoluble surface oxide film. However, knowledge of the film composition under different oxidation conditions and at different alloy compositions is still insufficient to predict alloy behavior over a prolonged service lifetime. This work describes the chemical composition and structure of the films formed on Alloy 22 (Ni-Cr-Mo-W alloy) at different temperatures and applied potentials (E, cited versus SCE). Using ToF-SIMS, we have shown that the surface film comprises two layers with different compositions. The inner layer, in contact with the alloy, contains lower oxidation state oxides, such as Cr(III), Ni(II), Mo(IV), W(IV) oxides. The

outer layer incorporates Cr(III) and Ni(II) hydroxides, and, under the most oxidizing conditions, Mo(VI) and W(VI) oxides. An increase in formation potential leads to an increase in the film thickness.

XPS results showed that an increase in E from -0.4 V to 0.6 V leads to an increase in Cr and a decrease in Ni concentration, while the Mo concentration does not exhibit a strong potential dependence. An increase in T from 30° C to 70° C does not change this tendency, but the oxide surface becomes more depleted in Ni and enriched with Cr, suggesting that even at -0.4 V Ni leaching takes place.

High resolution XPS shows the Cr(III) oxide concentration rises until E = 0.2 V. At more positive E it is oxidized to Cr(VI), and dissolution of Ni(OH)₂ occurs, as the local pH value drops. The concentration of MoO₃ rises at higher E and it becomes the dominant molybdenum compound at E = 0.6 V for T < 70°C. At increased T it transforms to nonstoichiometric Mo₂O₅. Formation of Mo(VI) oxide (as well as WO₃), shows that the decrease in Cr₂O₃ concentration indicates destruction of the barrier layer. The subsequent formation of nonstoichiometric molybdenum oxide leads to much easier charge transfer through the film, due to an increase in the defect concentration in the molybdenum oxide structure.

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Corrosive Resistance of NiFe₂O₄ Based Cermet Inert Anodes in Low Temperature Electrolyte Na₃AlF₆-K₃AlF₆-AlF₃ for Aluminum Electrolysis

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The consumable carbon anode which is currently being used in the primary aluminum production has several disadvantages, including high carbon consumption (>400 kg/t Al), emission of CF_4 , SO_2 and polycyclic aromatic hydro-carbons. The implementation of non-consumable (inert) anode could solve these problems and has become a research focus for several decades. Among the materials studied as inert anode for aluminum electrolysis, NiFe₂O₄ based cermets were regarded as one of the most promising materials.

The use of low temperature bath can improve the service condition and reduce the corrosion rate of inert anode. So Na₃AlF₆-K₃AlF₆-AlF₃ saturated with alumina was used as low temperature electrolyte to test the corrosion resistance of Cu/(NiFe₂O₄-10NiO) cermet inert anodes in this work. Compared with the traditional Na₃AlF₆-AlF₃

electrolyte at 960°C, the corrosion rate of Cu/(NiFe2O4-10NiO) cermet inert anode in

low temperature electrolyte at 900°C decreases from 5.27 cm· a^{-1} to 0.85 cm· a^{-1} at an anode density of 0.95 A·cm⁻².

In the low temperature electrolysis with Cu/(NiFe $_2O_4$ -10NiO) cermet inert anode, the cell reaction is:

$$1/2Al_2O_3 \rightarrow Al + 3/4O_2 \tag{1}$$

However, there are several possible reactions competing with the cell reaction (1) under certain condition during electrolysis:

$$Fe^{2+} \rightarrow Fe^{3+}$$
 (2)

$$Fe^{3+} + NiO \rightarrow NiFe_2O_4$$
 (3)

$$Al_2O_3 + NiO \rightarrow NiAl_2O_4$$
 (4)

Thus, a passivation layer (Fig.1) with high density, which is advantageous to resist the corrosion of bath to inert anode, can come into being because the mol bulks of NiFe₂O₄ and NiAl₂O₄ are great than NiO existing in the ceramic matrix.

Ionic Transport and Durability of Advanced Thermal Barrier Coatings

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Thermal barrier coatings will be more aggressively designed to protect gas turbine engine hot-section components to meet future engine performance goals. Advanced low conductivity thermal barrier coatings have also been developed to achieve improved thermal stability and high temperature cyclic durability. A fundamental understanding of the sintering and oxidation thermal cycling behavior of the thermal barrier coating systems is of great importance for improving the coating system durability.

This presentation will focus on rare earth oxide alloyed $ZrO_2-Y_2O_3-Gd_2O_3-Yb_2O_3$ thermal barrier coatings with PtAl and/or NiCrAlY bond coat systems for achieving low thermal conductivity and improved cyclic oxidation resistance. The emphasis will be placed on the understanding of the oxide thermal barrier coating thermal sintering and phase stability, and bond coat oxidation mechanisms, along with the interactions associated with the ionic transport behavior within the oxide thermal barrier coating and bond coat systems. The effects of thermal barrier coating composition heterogeneity and cyclic environments (such as temperature and stress gradients) on the sintering and phase stability, as well as the Al_2O_3 oxide scale growth behavior on the thermal barrier coating system durability will also be discussed.

Initial Passive Film Breakdown on Crevice Wall for Iron in Near Neutral Sulfate/ Chromate Solution

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Experimental results are presented for the induction period that precedes the onset of crevice corrosion. The experimental system is iron in a sulfate/chromate solution of pH 9 at room temperature.^{1,2}



Visual examination and in-situ photography of the crevice wall revealed that the first breakdown of the passive film on the crevice wall occurs near the bottom of the crevice and has a roughly hemispherical shape not unlike that of a pit. The next attack is another pitlike corrosion cavity slightly closer to the crevice opening, then more pit-like cavities progressing up the wall until they merge into a horizontal boundary between the passive upper wall and lower corroded wall.

This latter morphology (horizontal boundary, etc.) is representative of stable crevice corrosion reported in earlier papers. During the induction period of passive-like behavior (micro-amp current) the measured baseline current is observed to increase gradually and only at a later time does the current increase much more steeply with time during stable crevice corrosion. During the induction period there are some small current spikes (current increases then decreases) in the baseline current.

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Poster Presentations



Sustainability of Composite Zinc and Zinc Based Deposits Additionally Treated in Environmentally Friendly Conversion Solution

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The increasing demand of new protective materials against corrosion leads to elaborating of new approaches. For example, zinc electrodeposition is an industrial process of high importance since this metal corrodes in natural environments by a factor of 10 to 100 times less than steel. Therefore, a variety of methods and techniques are available for improving the zinc coatings performance e.g. alloying with other metals, conversion coatings, composite coatings, etc.

The corrosion resistance of a galvanic zinc layer depends, among other factors, also on the morphology and crystallographic orientation in the layer. For example, particular grain refinement of the zinc layer may be achieved by incorporating polymeric nanosized aggregates, which on one hand act as new nucleation sites and on the other hand, increase the corrosion resistance due to the amphiphilic nature of the used polymer.

The main objective of the present work is to investigate the electrochemical properties and corrosion performance of composite zinc and Zn-Co coatings, incorporating stabilized polymeric micelles (SPMs) from amphiphilic PEO₇₅PPO₃₀PEO₇₅ tri-block copolymer, in comparison with pure galvanic zinc and Zn-Co in 5% NaCl solution as a model medium. Since the composite coatings contain practically insoluble polymeric micelles with nano-sizes and metallic grains, an altered metal matrix and increased barrier properties could be expected.

Using CVA curves it was established that SPMs affect significantly both the cathodic and anodic processes by shifting the potential maximums and changing their shapes. SEM investigations give more information about the surface morphology status of the composites as well as of the galvanic deposits. XRD investigations of the texture and the corresponding changes in the corrosion behavior are explained and discussed. Based on the obtained results some multilayer systems consisting of composite and galvanic coatings are created and characterized.

In order to increase the sustainability of the deposits and of the newly developed multilayer systems an additional treatment in environmentally friendly Cr^{3+} -based solution for a short period of time was applied. The conversion coatings obtained demonstrate higher polarization resistance in the model corrosion medium.

Further, the mechanism of the incorporation of the SPMs in the metal and alloy matrix, as well as the phenomena, related to the increased barrier properties and a kind of "self-healing" action of the composite and conversion coating in the event of corrosion attack, are also discussed.

Effect on Time-To-Corrosion of Chloride-Induced Corrosion of Reinforced Concrete Structures

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Corrosion of reinforcement is the main cause of failure of concrete structures [1]. In order to prevent and delay rebar corrosion, a high quality concrete with a proper concrete cover and a good mix proportion should to be designed. Additional prevention methods are adopted when severe environmental conditions occur, or on structures requiring very long service life, as well as in rehabilitation [1]. Among available methods, corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared to other preventive methods [2].

The paper reports the results of a ten-year investigation on the effectiveness of three commercial organic inhibitors and some new organic compounds in preventing chloride–induced corrosion. Tested organic compounds are amine and carboxylate based. They were selected among about 80 organic substances trough electrochemical tests performed in alkaline pore simulated solution [3]: potentiodynamic polarization tests, potentiostatic polarization tests and free-corrosion tests.

The effectiveness of the commercial inhibitors and the selected organics were evaluated by long-term rebar corrosion monitoring in reinforced concrete, and by rebar visual inspection after testing. Concrete specimens were exposed to accelerate chlorides penetration by means of ponding cycles (1 week wetting with 3.5% NaCl solution, 2 weeks drying). The results provide useful information on the corrosion prevention ability of the tested inhibitors: the effect on time-to-corrosion has been studied analyzing the ability of inhibitors to increase critical chloride threshold and to decrease chloride penetration rate.

Based on the obtained results, the increase of time-to-corrosion has been evaluated by means of a Montecarlo simulation. The following scenario has been compared: standard concrete cast with Portland cement and carbon steel reinforcements; use of stainless steel rebars; use of blended cements; use of inhibitor able to increase critical chloride threshold; use of inhibitor able to reduce chloride penetration rate.

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Effects of Ozone and UV on Polymer Coating Degradation and Corrosion of Metal Substrates

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Accelerated laboratory exposures are used to predict and understand the degradation of polymer coated metals in the life of their service. However, there are some discrepancies between laboratory exposure and field exposure. Laboratory tests have the advantage of controlling and studying parameters like UV, relative humidity, temperature, SO_x and other pollution that drive the degradation of the polymer coated metals. This study focuses on the effect of O_3/UV and polymer coated metal photo degradation. The coatings studied are the Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB) and Eponol TM/53-BH-35 B, both are applied on AA2024-T3. The photo decomposition of ozone in presence of water forms hydroxyl radicals that react with the sample surface. The chemical degradation of the polymer is analyzed with IR-spectroscopy. The carbonyl peaks at 1717 cm⁻¹ for PVB and 1721 cm⁻¹ for Epanol might measure the coating degradation extent. The chemical degradation is correlated with electrochemical study (EIS, SKP) and with mechanical study (Nano-indentation, Pull-off test).

Corrosion and Cracking of Carbon Steel in Fuel Grade Ethanol – Exploration of Supporting Electrolyte

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Carbon steel has been observed to be susceptible of stress corrosion cracking (SCC) in fuel ethanol environment, which is used to fabricate storage tanks and pipelines. It is a big challenge to existing storage and transportation system of fuel grade ethanol (FGE) with increasing extensive usage of biofuel. Dissolved oxygen and corrosion potential are identified as the essential factors contributing to ethanol SCC. However, due to the limited understanding of SCC of carbon steel in ethanol, a gap exists in the guidelines for mitigating SCC risk. The investigation of the electrochemical response of carbon steel in FGE is essential to develop a mechanistic understanding of SCC process with influences from different sources and additives. Another challenge that results from implementing electrochemical measurement in ethanol solutions is its high electrical resistivity. Adding non-complexing supporting electrolyte is considered to be the most practical method to carry out any measurements at controlled potential, including slow strain rate (SSR) tests. In order to find an ideal supporting electrolyte in ethanol solution, a series of cyclic potentiodynamic polarization and electrochemical impedance spectrum tests were performed on carbon steel specimens in the simulated fuel grade ethanol (SFGE) with a variety of salt candidates, both under aerated and deaerated conditions. Not many salts commonly used as supporting electrolytes are soluble in ethanol solution. Lithium perchlorate, lithium chloride, lithium iodide, lithium nitrate, and tetrabutylammonium tetrafluoroborate were chosen to explore their electrochemical performance besides decreasing solution resistance. Furthermore, the micro-electrode technique was applied to verify the effects of the supporting electrolyte, by comparing the electrochemical response of carbon steel in SFGE with or without these supporting electrolytes. A suitable supporting electrolyte without any influence on electrochemical process is essential to study corrosion phenomena in organic media.

Electropolishing of Niobium to Obtain Defect Free Surface

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Pure niobium is considered the best metal for making superconducting RF cavities. However, good performance of the cavities is strongly dependent on their surface finish. Electropolishing can be used to give a good surface finish to the Nb surface. The basic process for electropolishing of these cavities exists but, because of lack of control of some process parameters, some unexpected defects are associated with the electronbeam welded region of the RF cavities. These defects lead to a reduction in the performance of the SRF cavities. The primary aim of our research is to understand the basic mechanism of electropolishing of Nb and control the parameters employed in the processing of SRF cavities.

The best polishing conditions for electropolishing are determined by polarizing the surface to different potentials and then determining the surface conditions obtained. The best voltage is expected to be in the plateau region of the I-V characteristic for Nb. The important parameters affecting the plateau region are acid concentration, electrolytic temperature, viscosity and stirring. The effect of these parameters are studied using flat niobium specimens with high purity Al as the cathode. The electrolyte used is a mixture of 1 vol HF (48%) and 9 vol H_2SO_4 (95-98%). The samples are characterized using optical microscopy, SEM and AFM for surface roughness and pits.

Another electrolyte recipe with the addition of a small volume of lactic acid is expected to give a higher polishing rate. The effect of distance between the electrodes will be studied. EIS is used to determine the mechanism of electropolishing. A special electrolytic cell design with the electrodes shape simulating the actual cavity geometry will be used and the processing parameters obtained from the flat specimens adjusted accordingly. The results from all the above experiments will allow development of the parameters for the best electropolishing conditions of the actual SRF cavities.

Corrosion Resistance Assessment of Pre-Treated Magnesium Alloys

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Magnesium alloy has been desired for automobile industries due to its light weight, which could increase fuel efficiency and save energy. However due to its activity, it has high tendency to corrode in the aqueous environment. The goal is to constitute a protocol for testing the corrosion rate for matrix alloy and conversion coatings. Three base magnesium alloys AM60, AM30, and AZ31 have been tested for intrinsic base metal corrosion rate, and 6 pre-treated conversion coatings have been tested for corrosion resistance performance. Electrochemical tests (open circuit potential and potentiodynamic polarization) are used to quantitatively differentiate the corrosion potential, corrosion rate, and passivity for each coating. Salt spray exposure tests are used as a qualitative assessment of the performance of the coatings. The microstructure has also been investigated for the relationship between the microstructure and the intrinsic corrosion rate. The results show that AM60 has the lowest intrinsic corrosion rate while phosphor based conversion coating has best corrosion resistance.

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Evaluation of the cathodic inhibition by rare earth (Ce³⁺, Pr³⁺, La³⁺) and Zn²⁺ cations on AA 2024-T3 alloy and characterization of cation exchanged bentonite pigments dispersed in organic coatings.

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A comparative study of the corrosion inhibition caused by rare earth metal cations, Ce^{3+} , Pr^{3+} , La^{3+} and Zn^{2+} cation on high strength AA 2024-T3 alloy was done. Cathodic polarization showed that these inhibitor ions suppress the oxygen reduction reaction (ORR) to varying extents. It was verified that Ce^{3+} and Pr^{3+} exhibit windows of concentration (100-300 ppm) in which the corrosion rate is minimium. Among all the inhibitors, Zn^{2+} is a better inhibitor of the ORR and a critical concentration of 325 ppm is required to produce maximum inhibition. Rotating disk electrode experiments on Cu showed a two order of magnitude reduction of the cathodic current in the presence of $ImM Zn^{2+}$. SEM studies showed that the mechanism of inhibition of the Pr^{3+} ion is seen to be similar to that of the Ce^{3+} ion. The sample in Zn^{2+} bearing solution, showed thread-like structures (may be Al-Zn hydrotalcites) on the entire surface and trenching attack around the intermetallics.

The inhibitor ions were exchanged into insoluble sodium bentonites and incorporated as pigments in non-protective organic coatings on AA 2024-T3 substrates. XRD of the pigments ensured ion exchange and UV-vis spectroscopy was performed to ensure inhibitor release from the bentonites. None of the coated samples showed scribe protection in the salt spray tests. Electrochemical Impedance measurements showed increased coating degradation after 24 hrs of static immersion. Neat polyvinyl butryal (PVB) coated sample showed better barrier properties than those with pigments.

The Records of Atmospheric Corrosion Study: Facts and Figures

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Corrosion phenomena are as old as history of materials and the demand for corrosion research has been drastically increased. Problems of atmospheric corrosion were recognized as a critical importance early in 19th century, and attention was given to explaining this phenomenon. Little progress was made until the beginning of the last century when the electrochemical concepts were applied to corrosion problems. A dramatic increase was observed in 1960s, and nothing is expected to change the tendency over the time, as shown in figure.



The aim of this paper is to introduce the references describing the atmospheric corrosion. This involves the distribution and discussion across publications, covering systematic area of research, experimental techniques and methods, including simulation and modeling, and laboratory and actual service testing. Reference dynamics are examined by quantifying annual production into each area, and the evaluation of each level is also discussed.

Also, this communication details how researchers from over the world are developing new tools that are useful in the study of corrosion. The tools developed are the ways that provide the framework for understanding the nature of atmospheric corrosion. In addition, it is furthermore able to provide methods of protection, or methods designed to keep corrosion within reasonable limits.

Long Term Stability of a multilayer green coating

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In present, the zinc multilayer coatings passivated with non-toxic substances are very much used: so, the coating with phosphated zinc [1,2] protects the carbon steel against corrosion in alkaline media; zinc-molybdate [2] and zinc- molybdate-phosphate - silicate [2] coatings are compact and assure protection in acid and alkaline media; zinc-chromium coatings (III) [3] presented very good performances for long periods.

In this paper is studied a multilayer coating based on zinc passivated with chromium (III); zinc protection were deposited from un-polluted alkaline bath and passivation was realized with non-toxic chromium compounds (III), therefore these protections are unpolluted, "green" coatings.

The experiments were carried out in synthetic sea water (ASTM D 1141-98). Electrochemical techniques of potentiodynamic and linear polarization, electrochemical impedance spectroscopy and monitoring of open circuit potentials were used.

The presence of Cr (III) compounds in passivated layer over the zinc coating determined slight more electropositive values of the corrosion potential, more reduced passivity currents and high polarization resistances; these facts prove the improvement of the protective capacity of this multilayer coating. Corrosion rates decreased very much for carbon steel coated with passivated zinc layer due to benefic effect of passivation with chromium; these rates decreased very much in time proving that, the protective performances of the coating increased (Table 1).

Material	Time (h)	E _{corr} (mV)	i_{corr} ($\mu A/cm^2$)	V _{corr} (mm/an)	R_p (k Ω .cm ²)
Carbon steel	500	-742.2	22.34	0.173	642.75
	1000	-753.1	31.68	0.245	534.94
	3000	-770.9	43.32	0.335	516.92
	5000	-780,0	59,03	0,502	485,42
Carbon steel + multilayer coating	500	-1141.1	9.98	0.149	822.46
	1000	-1135.4	3.03	0.045	1160.15
	3000	-1130.8	0.69	0.015	3190.24
	5000	-1116,4	0,21	0,010	3305,12

Table 1 Corrosion rates of multilayer coating in sea water at 23^oC

Also, it resulted that, the open circuit potential tend to more electropositive values in time, showing that passive layer with Cr (III) from multilayer coating has effect of increase of the coating protective properties.

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Corrosion Monitoring of Carbon Steel Substrate Coated with a New Paint Film

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The paint films are generally not impervious barriers to corrosive reactants (water, water vapors, oxygen and ions) and therefore the corrosion process can develop through and under paint film. Their permeability depends on: the paint composition, the deposition technique of the film and its thickness.

This paper presents the results of the corrosion monitoring of carbon steel substrate coated with a new alkyd paint film with low content of volatile organic compounds (VOC - 4-5%) in comparison with a conventional alkyd paint (VOC - 45-46%); the electrochemical measurements (electrochemical impedance spectroscopy - EIS; potentiodynamic and linear polarization) and the surface analysis (atomic force microscopy - AFM, scanning electron microscopy - SEM and energy dispersive analysis - EDX) were used. The experiments were conducted in 3% NaCl solution at 23^{0} C, for a period of up to 1500 immersion hours.



Modeling (two time constant electric equivalent circuit) and time monitoring of metal/organic film interface has permitted to determine the presence of double layer under paint film, the active area of the metallic surface, the corrosion rate, water uptake and area of the conductive pathways in coating

The corrosion processes at the carbon steel/coating interface were evaluated using the charge transfer resistance and the double layer capacitance; time evolution of the double layer capacitance showed that the wet metal area under coating is more reduced for the alkyd paint with low content of VOC; time trend of the charge transfer resistance standed out that the electrochemical reactions at this interface were slightly slowed down for the alkyd paint with low content of VOC than for conventional paint.



The new studied paint film presents a good adhesion to the carbon steel substrate; during the exposure period no degradation or delamination process could be observed. The surface analysis with AFM revealed: a compact coating without pores (three-dimensional image in figure).

SEM micrographs showed that, before immersion the coating is homogenous and adherent and after 1500 immersion hours did not appear important changes. EDX elemental analysis detected the same constituent elements both before immersion and after 1500 immersion hours, proving that the paint film is resistant and did not degrade. Efficiency of the protective film was calculated. It results that the alkyd film with low VOC content presents good performances; its efficiency does not decrease in time below 90%.

Effect of components in soy sauce on the corrosion behavior of various stainless steels

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Manufacturing plants for soy sauce is exposed to severe corrosive environment of highly concentrated sodium chloride containing various organic compounds. Therefore, the evaluation of corrosion resistance for stainless steel is the essential factor for equipment to be use in manufacturing process in such conditions. Especially the interior metal surface of the tank is exposed to severe corrosive environment of highly concentrated sodium chloride containing various organic compounds. Moreover, the exterior metal surface of the tank is exposed to severe corrosive environment of extremely warm and humidness. Practically, the annual cost is so expensive for maintenance and that time takes so long by the corrosion damage in many soy sauce manufacturing.

The cause of these increasing tendencies is tanks specification. Many exiting tanks specification is constructed from carbon steel to cover with resin. For the corrosion process of tanks, after the resin on the surface of tank is destroyed by heat or mechanical shock in production process, aging of resin, the corrosion rapidly destroys the structure of tank. Therefore, tanks specification makes immediate a switch from carbon steel with resin to stainless steels due to the stabilization of process, product quality and cost reduction for plant maintenance.

On the other hand, unfortunately, not very much is known about the corrosion behavior of industrial stainless steels in soy sauce manufacturing plants, although a few reports are available on the immersion test and pitting potential in soy sauce and moromi.

And then, the evaluation of corrosion resistance for stainless steels is the essential factor for equipment are pitting and crevice corrosion, even stress corrosion cracking in such conditions. Consequently, this paper was developed the corrosion resistance by electrochemical measurement method for various stainless steels in soy sauce environment, the effects of components in soy sauce such as several organic acids aqueous solutions, Sodium Chloride aqueous solutions and their mixture for corrosion resistance to various stainless steels.

For experiment, test specimens are used several austenitic stainless steel and duplex stainless steels. The effect of pitting corrosion and passivation layer on metal surface is investigated by electrochemical anodic polarization and impedance measurement in wide temperature($303K \sim 363K$).

It has been shown that the result is basic date to evaluate for the corrosion resistance of various stainless steels in soy sauce. The detailed results will be discussed in proceeding.

Raman Analysis of Surface Vanadate Species on the Matrix and Copper-rich Intermetallic Particles of AA 2024-T3 Alloy Treated with NaVO₃ and NH₄VO₃

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Raman spectroscopy was used to analyze the surface film formed on AA 2024-T3 alloy treated with aqueous solutions of NaVO₃ and NaCl and aqueous solutions of NH₄VO₃ and oxalic acid. Additionally, films formed on bare copper (Cu⁰) and on cuprous oxide (Cu₂O) treated with aqueous NaVO₃ were used as a model for the copper-rich intermetallic particles found in AA 2024-T3. Raman analysis indicated the presence of a polymerized vanadate film on both the matrix of AA 2024-T3 and its copper-rich intermetallic particles when treated with an aqueous NaVO₃ and NaCl solution. This is in agreement with the Raman analysis of Cu₂O treated with aqueous NaVO₃ which indicated a similar polymerized vanadate film. Raman analysis of bare copper treated with aqueous NaVO₃ showed no evidence of any vanadate species on the bare copper. Raman analysis of AA 2024-T3 alloy treated with an aqueous NH₄VO₃ and oxalic acid solution indicated the presence of a polymerized vanadate film and, additionally, the presence of individual tetrahedral vanadate units on intermetallic particles.

Cathodic polarization scans performed in aerated 0.1 M NaCl solutions on AA 2024-T3 alloy samples treated with aqueous NaVO₃ and NaCl solution and with aqueous NH₄VO₃ and oxalic acid solution both showed similar, mild inhibition of the oxygen reduction reaction.

Influence of thermal treatment temperature on the passivating efficiency of interference colored stainless steel

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The deposition of interference thin films on the surface of stainless steel is a method for enhancing the decorative and architectural application of this material. A wide variety of interference colors, including brown, blue, gold, purple, and green, can be obtained, in this sequence, as the film thickness is increased from tenths of nanometers to one half of a micrometer[1]. Further, this thin passivation layer on stainless steel improves its surface properties, increasing the number of applications[2].

The characteristics of colored interference thin films on stainless steel were investigated by thermally treating these films at 150, 350, 650 and 950C °C for 2hours. The thermally treated films were morphologically characterized using field emission scanning electron microscopy (FESEM). Film nanohardness was evaluated by depth sensing nanoindentation. The film structure was studied by DRX and the electrical resistivity by a linear sweep voltametry method. The passivity behavior was investigated by EIS at the open circuit potencial in borate buffer solution (pH 8.4).

An amorphous structure was observed for the interference films, but a film crystallization after thermal treatment was identified (Fig. 1) in the diffraction peaks corresponding to α -Cr₂O₃ and γ -Cr₂O₃observed in the 650^oC and 950^oC samples, respectively. The highest hardness value was observed for the 650^oC sample, which can be associated with the α -Cr₂O₃ corundum phase. On the other hand the highest electrical resistivity was observed for the 950^oC sample. Evaluation of EIS data suggest a tendency to a more capacitive behavior at the low frequency as the thermal treatment temperatures increases.



Fig.1. Interference film morphology after thermal treatment at 950° C (a)and 150° C (b). The transformation in the structure of the oxides generates a less conductive film and, as a consequence, an increase in the low frequency limit of the impedance.

Assessment of the Viability of Simulating Corrosion Fatigue in Sour Environments with S₂O₃²⁻ Solutions

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The integrity of risers and pipelines used for deep water oil extraction can be limited by corrosion fatigue. Hydrogen sulfide, H_2S , can dramatically increase the kinetics of this degradation mechanism, since it increases the hydrogen absorption and the corrosion rate of carbon steels. Testing of materials in this environment is expensive due to the toxicity, flammability and corrosive character of this gas, which requires the use of special installations to ensure safety.

An interesting alternative is the use of substances that can produce H_2S locally at the metallic surface. Thiosulfate is a non toxic, water soluble ion that can react to yield H_2S in a broad range of pH and potential. If it could be shown that behavior in thiosulfate solutions reproduces the behavior in hydrogen sulfide solutions, sour corrosion fatigue testing would be simplified enormously.

Little work has been done on electrochemistry of steels in thiosulfate solutions. Therefore, a project aimed to determine the corrosion and hydrogen absorption kinetics of pipeline steel in thiosulfate-substituted NACE TM0177-90 solutions (5wt% NaCl + 0.5wt% acetic with small thiosulfate additions, instead of H₂S saturation) was started. Corrosion fatigue testing in those solutions and the comparison of crack growth rate against hydrogen sulfide results will allow selection of the most appropriate substitute solutions, while yielding data about relative contributions from hydrogen absorption and enhanced anodic dissolution.

The figure below shows the results of cathodic potentiodynamic polarization at a scanning rate of 0.2 mV.s⁻¹ in 5wt% NaCl acidified with 0.5wt% acetic acid (HAc), with and without a 10^{-2} M addition of sodium thiosulfate. Low carbon steel samples were polished to 600 grit prior to running the tests. Solutions were deareated to prevent oxidation of the thiosulfate ion. An increase in cathodic reaction rate and corrosion current is evident, despite the small concentration of the sulfur containing ion.



Figure 1. Potentiodynamic polarization curves with and without thiosulfate addition in NACE TM0177-90 substitute solutions.

Development of an Electrochemical Method of Detection of Sensitization in Al-Mg Alloys

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Al-Mg allovs (AA 5XXX) are attractive for use in the hulls and structural members of high-speed ships because of their high strength-to-weight ratio, cost, and availability. Unfortunately, at temperatures as low as 70°C, the formation of a beta-phase (Mg₂Al₃) occurs along the grain boundaries, and that phase facilitates intergranular corrosion that leads to cracking. This phenomenon is known as sensitization. Currently, the only means of quantifying sensitization responsible for intergranular corrosion 5XXX aluminum alloys consists of a destructive nitric acid mass-loss test, ASTM G-67 which requires 24 hours of testing time. For timelier repair/replacement decisions, a rapid, non-destructive method is needed. This work has focused on the development of an electrochemical method for the detection of sensitization in 5XXX aluminum alloys. The experimental procedure for measuring the DoS consists of exposing the AA5456-H116 to a pH 11 commercially certified phosphate buffer solution and conducting a thirty-minute open-circuit potential (OCP) measurement, followed by a thirty-minute potentiostatic hold, and concluding with a fifteen-minute OCP measurement. The time course of the final OCP measurement has been shown to reflect the DoS level of the AA5456 material, as determined by ASTM G-67 testing. The method relies on the fact that the Al-Mg matrix and the Mg_2Al_3 exhibit very different electrochemical behavior under some conditions. In particular, it is expected that at low and neutral pH, the Mg₂Al₃ will be active, whereas the Al-Mg matrix will be passive, while at high pH, the opposite behavior will be observed. Measurement of the open circuit decay of the system after a passivation treatment allows differentiation of the degree of sensitization due to the area ratio (Al-Mg: Mg₂Al₃) differences that develop during sensitization. The majority of the work has considered AA5456, an alloy historically used widely in naval superstructures, but the method has been extended to other more modern alloys (AA5083, AA5086). This work will report on the effect of pH, composition of the electrolyte solution, surface condition, and the alloy being tested on the electrochemical parameters measured.

Corrosion and passivation of Fe-Cr alloys in geothermal water

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One of the major problems connected with the exploitation of geothermal hot water fields is corrosion of the thermal water installation. Thermal water is chemically aggressive system of $H_2O-CO_2-H_2S$. Choice of proper corrosion resistant materials for pipes, fittings and heat exchangers is essential for correct and economical operation as well of geothermal wells as of surface exploitation systems.

The aim of the work was to present the mechanisms of anodic dissolution and corrosion of Fe-Cr alloys in geothermal water of Geotermia Podhalańska S.A. (low salinity system of $H_2O-CO_2-H_2S$) and Geotermia Stargard S.A. (high salinity system of $H_2O-CO_2-H_2S$). Our investigations of the corrosion behaviour of low-chromium steels, performed in field conditions, in operating geothermal heating plants, and in laboratory experiments, at elevated temperature and high pressure, revealed that the corrosion rate falls nearly exponentially with chromium content in the steel.

Electrochemical investigations, of Fe-Cr alloys (1 to 5%Cr) and low alloyed steels performed in laboratory and in field conditions, show that the corrosion of these materials in H₂O-CO₂-H₂S system proceeds in the active or prepassive range and is controlled by protective properties of insoluble surface layer of corrosion product. SEM and EDX analysis of carbon steel and low chromium steels (1 to 5%Cr), exposed in Geotermia Podhalańska, indicates that the surface product consists mainly of magnetite, mackinavite (FeS_{1-x}) and small amounts of siderite FeCO₃. The layer becomes more compact, homogeneous and fine-crystalline with increase of chromium content in the alloy. It appears that low amounts of Cr stimulate the formation of dense well fitting to the metal surface anodic film. Potentiostatic transient experiments and electrochemical impedance measurements, performed on pure Fe-Cr ferrite alloys, show that the time of formation of surface layer decreases with increase of chromium concentration in the alloy. It seems that the high activity of chromium in the first seconds of anodic etching enhances oversaturation of metal surface in anodic product, and promotes nucleation of anodic layer. Even negligible chromium content in the ferrite matrix acts as modifier of formation of protective layer of iron surface compounds (magnetite, sulphide).

The corrosion rate Fe-Cr alloys depends also on the steel microstructure. Field experiments (LSV, EIS) and laboratory measurements (micro-electrochemical investigations) show that the eutectic phase with fine dispersed carbides (perlite) shows higher corrosion resistance than ferrite or martensite one. High dispersion of cathodic phases (carbides) promotes oversaturation of ferrite matrix in anodic product and nucleation of protective layer of anodic product.

Effects of Solution Temperature on the Passivity of Nickel

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Corrosion behaviors of a passive metal is degraded with an increase in solution temperature; passive current density of a passive metal increases with temperature. In spite of numerous studies on the influence of temperature on the corrosion behaviors of passive metals and their alloys $[1\sim2]$, the mechanism how the solution temperature affects the corrosion behavior of passive metal remains unclear. Therefore, the present work is to provide further understandings of effects of solution temperature on the corrosion behaviors of passive Ni, one of the metals with p-type passive film, in terms of the kinetic parameters of interfacial reactions and diffusivity of point defects.

In this study, we examined the effects of temperature on the defect structure of passive film on Ni using Mott-Schottky analysis, and explored the kinetic nature of the electrochemical reactions occurring at the metal/film/solution interfaces based on point defect model (PDM) by electrochemical impedance spectroscopy (EIS).

Polarization response of Ni (99.99%) measured in pH 8.5 buffer solution at 30, 50 and 80°C, respectively, shows that the passive current density of Ni significantly increases with an increase in the solution temperature.

The kinetic rate constants for the interfacial reactions and the diffusivity of cation vacancy in the passive films of Ni were extracted by optimizing the PDM on impedance data measured at 30, 50 and 80°C. Under the steady state condition, the current density through the passive film on Ni is associated with cation vacancy flux

 $(I_{SS} \approx FIJ_{VN})$ in the passive film. With increasing temperature, the cation vacancy generation rate at the film/solution (f/s) interface increased significantly, thereby increasing the cation vacancy flux at the f/s interface. Because diffusivity of cation vacancy was significantly enhanced by solution temperature, the cation vacancy generated at the f/s interface moved to the metal/film (m/f) interfaces more rapidly. While the annihilation rate of cation vacancy decreased with increasing temperature, the cation vacancy concentration at the m/f interface increased more abruptly with temperature, thereby increasing the cation vacancy flux at the m/f interface. The increase in the cation vacancy flux in the passive film resulted in the increase of I_{SS} . According to the PDM, film breakdown is closely associated with cation vacancy condensation at the m/f interface. The cation vacancy concentration at the m/f interface at the m/f interface increased drastically with solution temperature. Therefore, it is suggested that the possibility of formation of "vacancy condensate" increases with solution temperature.

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Chromium Passivity in Sulfuric Acid Solution

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Passivity of chromium in 0.5 M sulfuric acid has been explored using cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy. The results of potentiostatic measurements have shown that the passive current density is potential-independent, while the thickness of the passive layer increases linearly on the applied potential, which is consistent with the postulation of the Point Defect Model.

The Mott-Schottky analysis revealed that the passive film is an *n*-type semiconductor (related to the outer $Cr(OH)_3$ layer). No evidence for *p*-type behavior was obtained, indicating that the cation vacancies do not have a significant population density in the film compared with the two donors (cation interstitial and oxygen vacancies).

The transpassive state comprise a thick, porous oxide film on the surface, with characteristics consistent with the oxidative ejection of Cr(VI) species from the barrier layer.

Study of Corrosion of Carbon Steel at the Liquid-Air Interface in Simulated Nuclear Waste Solutions

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Millions of gallons of high-level liquid radioactive waste from the production of nuclear weapons are being stored temporarily in underground carbon steel tanks at selected sites. There is a deep concern that the corrosion failure of the tanks caused by aggressive aqueous waste solutions would cause unacceptable public radioactive exposure. Localized corrosion at the liquid-air interface (LAI) has been confirmed in the laboratory tests under certain conditions. However, no evidence for LAI corrosion has been observed in the real tanks. The mechanism responsible for the LAI corrosion observed in the lab has not been elucidated and is the focus of this work.

LAI corrosion was investigated on 1018 plain carbon steel samples partially immersed in simple simulated alkaline nuclear waste solutions containing sodium nitrate and sodium nitrite. Electrochemical measurements were conducted to evaluate the effects of pH, ion concentration and aeration/deaeration on the initiation of LAI corrosion under applied anodic potential at room temperature. LAI corrosion was always initiated exactly from the very top of meniscus region under conditions of strong passivity with high pH and high nitrite/nitrate concentration ratio. If the environment was less passive, localized or general corrosion also occurred at locations below the waterline. To further understand the mechanisms of the LAI corrosion, Raman spectroscopy was used to in-situ monitor chemistry changes during the LAI corrosion process under applied anodic potential. The results showed that the un-normalized peak intensity of nitrate ions does experience a change. The nitrate ion peak intensity was unchanged at the beginning of the test for certain time. During the initiation time for LAI corrosion, the nitrate ion peak started to shift to higher intensity. However, it declined back to lower intensity once the LAI corrosion experienced apparent rapid growth. The peak intensity change indicated that nitrate ion concentration was changing, which will be investigated more accurately in the future work. Moreover, the change in nitrite concentration has not been identified at this point due to unexpected difficulties, which is also essential for clarifying the LAI corrosion mechanisms and will be investigated further.

The Effect of Ozone on Atmospheric Corrosion of Copper in the Presence of NaCl Particles

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Ozone is one of the most corrosive gases in the atmosphere. Its effect on atmospheric corrosion of various metals has been reported by a number of groups around the world. Interaction of ozone with ultraviolet radiation (254 nm) generates $O(^{1}D)$, an excited oxygen atom. This excited oxygen atom can react with water to generate hydroxyl radical (OH). Excited oxygen atoms and hydroxyl radicals are species that can have a large impact on atmospheric corrosion of different metals, especially if present in accelerated exposure experiments in which pollutant particles are absent. Recently it was reported that hydroxyl radical can react with sea salt aerosols to generate corrosive molecular chlorine. Therefore, it of interest to understand the roles of both corrosive particles and ozone during lab exposure experiments for atmospheric corrosion research.

This poster presents research on the combined effects of ozone, UV, sodium chloride and relative humidity on the atmospheric corrosion behavior of copper. Sodium chloride was preloaded onto copper surface by thermophoretic deposition. After that, copper was exposed in a chamber with different controlled environments. Corrosion products were identified by XRD and XPS and quantified by galvanostatic reduction in 0.1 M KCl. The corrosion product was found to contain both copper chloride and cuprous oxide. Different exposure environments produced different corrosion products. The quantity of corrosion products increased with ozone concentration (from 250 ppb to 900 ppb) and relative humidity (from 0% to 90%). In the absence of sodium chloride, the corrosion rate was very slow even in a high ozone concentration environment (8 ppm). This could prove that the reaction of hydroxyl radical and chlorine ion to generate molecular chlorine is an important step for atmospheric corrosion of copper.
A study on interaction between macrocell and microcell in an early corrosion process of reinforcing steel in concrete

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As development of diversiform construction and service conditions in the past decades, the environments induced corrosion and premature degradation of steel reinforced concrete structures becomes increasingly serious and ubiquitous, which has been recognized as a difficult and frontier issues in the world. The durability and safety of the large-scale or key rebar reinforced constructions are highly concerned. It is well known that the essential reason for the premature degradation of reinforced concrete structures is corrosion of steel rebar in concrete, which is a typical electrochemical process happened in an occluded system.

An array electrode technique was developed as a novel electrochemical method for studying the interaction between macrocell and microcell in the early corrosion process of reinforcing steel in cement mortar. The corrosion potential and galvanic current of macrocell corrosion of the reinforcing steel in cement mortar were imaged by the array electrode technique during the corrosion initiation and propagation. It was certified that the corrosion macrocell current is closely related with the difference of corrosion potential between the anodic and cathodic areas. The corrosion macrocell and microcell always exists during the corrosion process. The interaction of corrosion macrocell and corrosion microcell of steel in concrete was directly sensed by the array electrode (Fig.1), and discussed in the aspect of corrosion electrochemistry.



Fig.1 Maps of corrosion potential distribution of steel rebar in concrete by immersing of an array electrode in 3.5% NaCl solution at different time. (a) 20 d; (b) 48 d

Inhibition of Aluminum Alloy 2024 by Selected Inhibitors in Solution

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The inhibition of aluminum alloy by sodium molybdate and sodium decanoate, a longchain carboxylic acid, was investigated by in situ atomic force microscopy (AFM) scratching. This technique is used to analyze the early stages of corrosion at selected sites with sub-microscopic resolution. For years, molybdate has been used as an inhibitor due to its low toxicity. Sodium decanoate, an organic inhibitor, has been recently found to act as a corrosion inhibitor to AA2024 by forming a hydrophobic film on the metal surface. Electrochemical experiments were used to characterize the inhibition mechanism by varying the pH, as well as the inhibitor and chloride concentrations. Both inhibitors experienced an increase in the pitting potential with incremental amounts of inhibitor concentration. AFM studies show that the addition of Molybdate to 0.5 M sodium chloride resulted in poor inhibition performance. Corrosion attack initiated after an hour of scratching at low tip forces. Attack nucleated at the periphery of the intermetallic phases, exhibiting similar kinetics of attack as in the case with no inhibitor. AFM studies on sodium decanoate are still ongoing and no conclusive results have been inferred thus far on its inhibition performance.

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Use of Limiting Current Measurements in Calibrating Annuli for Fluid Flow Studies at Elevated Temperatures and Pressures

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The calibration of an annular flow channel located inside an autoclave has been carried out by determining the limiting current densities $I_{L,ann}$ for the anodic oxidation of hydrogen as a function of the rotational velocity, N, of an impeller activating fluid flow through the annulus over tubular specimens mounted on the central column under electrochemical control. From the mass transfer correlation [1] given by the equation $St = 0.276 \ Re^{-0.42} \ Sc^{-0.666} \ (L/d_e)^{-0.333}$, where St is Stanton's number ($St = K_L/U_m$), Re is Reynold's number ($Re = U_m \ d_e /v$), Sc is Schmidt's number (Sc = v/D), K_L is the mass transfer coefficient, L is the electrode length, D is the reactant diffusivity (H₂), v is the kinematic viscosity, and d_e is the equivalent diameter of the channel (width of the annulus), an expression for the average flow velocity in the annular channel, U_m , can be obtained as:

$$U_m = 9.157 \, d_e^{0.1429} \, L^{0.5714} \, v^{0.4286} \, D^{-1.1429} K_L^{1.7144}.$$
(1)

Comparison of the I_{Lann} values measured for the mass transfer limited oxidation of hydrogen on platinized nickel in 0.1 M NaOH at a given temperature for various rotational velocities and calculated values of the limiting current density at a rotating disk electrode, $I_{L,disk}$, allows one to confirm the constancy of the value of $I_{L,ann}/I_{L,disk}$ ratio in the range of 400-1500 rpm and calculate U_m values for a chosen rotational velocity without the necessity of experimental determining $I_{L,ann}$ values. The determination of the temperature dependence of the $I_{L,ann}/I_{L,disk}$ ratio allows one to simplify the calculation of U_m for any temperature in the studied range of temperature and for any rotation speed. This procedure leads to the complete characterization of the hydrodynamic and mass transport properties of the channel, rendering the channel ideal for accurate electrochemical and corrosion studies. For example, this cell has been used to explore the kinetics of the hydrogen electrode reaction at temperatures from 22 °C to 200 °C, to explore the passivity of zirconium in simulated BWR and PWR primary coolant circuit environments at temperatures to 250 °C, to explore the growth and reduction of oxide films on platinum at elevated temperatures, to examine the effects of fluid flow on passivity breakdown and pitting on carbon steel and Alloy 600 at temperatures as high as 250 °C, and to explore the impact of amines on the passivity of ASTM A470/471 steel at 195 °C. Examples from these studies will be used to illustrate the application of the experimental system.

Kinetic Stability Diagrams and the Prediction of Passivity

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The use of reactive metals and their alloys (e.g., Ni-Cr-Mo-W-Fe and Fe-Cr-Ni alloys) for constructing machines that are exposed to ambient, corrosive environments relies upon a continuing state of kinetic passivity of the metal surface. Without this state, which is due to the formation and continued existence of a "passivating" oxide film, the alloy would react rapidly with components of the ambient environment (oxygen, water) and the structural integrity of the system would be compromised. The stability of the barrier oxide layers of bilayer passive films that form on metal and alloy surfaces, when in contact with oxidizing aqueous environments, is explored within the framework of the Point Defect Model (PDM) using phase-space analysis (PSA), in which the rate of growth of the barrier layer into the metal, (dL^+/dt) , and the barrier layer dissolution rate, (dL/dt), are plotted simultaneously against the barrier layer thickness. A point of intersection of dL^{2}/dt with dL^{4}/dt indicates the existence of a metastable barrier layer, with a steady state thickness that is greater than zero, and hence specifies the conditions that must be met for "passivity". The condition for passivity is stated simply as $dL/dt > (dL^+/dt)_{L=0}$. This formalism leads to the derivation of "Kinetic Stability Diagrams" (KSDs) for describing passivity in potential-pH space as alternatives to the classical Pourbaix diagrams. The KSDs describe the region in potential-pH space where the barrier layer of the passive film may exist as a metastable entity, noting that the layer can never exist as a thermodynamically stable entity, as proposed by Pourbaix.

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P-025

Investigation of defects in Mg-rich primer on AA2024-T3

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Mg-rich primers for aluminum were developed based on the mechanism of zinc-rich primers for steel. The more active magnesium pigments in the organic coating act as sacrificial anode for the aluminum substrate. Such behavior was observed employing several different electrochemical procedures [1-4]. However, details of the protection mechanism and the interaction of the coating and substrate are lacking. Therefore, AA2024-T3 was coated with commercial and self-prepared Mg-rich primer. A electrochemical Kelvin probe was used to measure potential profiles across defects in the coatings under a thin layer of 0.5 M NaCl and in dry conditions. In order to determine the electron flow between the Mg-rich primer and the aluminum substrate, galvanic corrosion experiments were conducted of bare and coated AA2024-T3 in dilute Harrison's solution.

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Poster Presentations

P-026

Corrosion prediction model enhancement for high pressure CO₂ environments

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The corrosion prediction model has been accepted as an important engineering tool for many applications such as new development strategy, current corrosion assessment, material selection and so forth. Recently it has been suggested that the current available tools will overestimate in prediction the corrosion rate at CO₂ partial pressure more than 20 bars. In this work present evidences that the actual corrosion rates are much less than predicted by a mechanistic model and empirical model. Most of the corrosion prediction models are able to predict corrosion rate close to the actual for CO_2 partial pressure below 10 bars. The present study also focuses on the modeling of corrosion rate as function of partial pressure of CO_2 up to 600 bars and temperature up to 100°C. Water and CO_2 mutual solubility study is precursors to the enhancement where it proved the deviation from ideal gas properties at high pressure condition thus Henry's gas law are no longer valid. Part of the present study is the determination of the solubility of CO_2 in water (xCO₂) over partial pressure of CO_2 up to 80 bars. Subsequence work cover the water chemistry study which quantified the species concentration of CO₂ (gas), CO₂ (aqueous), H₂CO₃, H⁺, HCO₃⁻ and CO₃²⁻ in the bulk solution system. The accuracy of this information is essential in predicting corrosion rate at higher CO_2 partial pressure and appropriate adjustment to the mechanistic model can be made.

Mass Transfer Characterization of Thin Channel Flow Cell for Flow-Sensitive CO₂ Corrosion Study

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At first glance, the need to explore for and develop hydrocarbon gas fields which contain high CO2 contents (up to 80 mole %) would call for use of expensive corrosion resistant alloys. This would have the potential to render project development costs that are untenable. An alternative approach would be to evaluate the technical feasibility of using carbon steels. Unlike transportation and sequestration of supercritical CO2, where the amount of water is normally negligible or comes from condensation, field development has to consider the presence of formation waters. These have the potential to contain multiple corrosive species. In addition to the action of such species during carbon steel corrosion, evaluations that involve the effect of flow on corrosion rates are required as flows have the possible effects of increasing corrosion rates. Flow-sensitive CO2 corrosion has been studied in rotating cylinder electrode (RCE) or pipe flow loop systems. In the present study, the effects will be evaluated using a high pressure and high temperature (HPHT) thin channel flow cell (TCFC); this has been designed and developed at ICMT. A key step of the study will be to characterize the mass transfer behavior in the TCFC; that is, to determine a Sherwood number that would indicate the power law upon which corrosion rates would be dependent on velocities. The mass transfer characterization was carried out at 30 °C and 50 °C, representing two different viscosities, and under various velocities. The experimental data seem to correlate well with the correlation of Sleicher and Rouse: $Sh=5 + 0.015Re^{a}Sc^{b}$.

Development of Porous Layer on Titanium Alloys Using Hydrogen Peroxide Solution for Orthopeadic Application

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Titanium is known for its biocompatibility and is widely used in dental and orthopedic reconstructive surgery. But, several reports indicated that osteointegration of these implants is not optimal. Thus, surface modification of titanium and its alloys to induce apatite deposition within a short period is of practical importance in clinical applications.

This paper presents a novel technology to enhance the biocompatibility and corrosion resistance of bio-inert α , $\alpha+\beta$ and β titanium alloys as implant material for orthopedic application. The surface of titanium and its alloys such as Ti, Ti-6Al-4V and Ti-15 Mo alloys were modified using 15 wt.% of hydrogen peroxide solution maintained at 80°C for 1 hr and then heat treated at 400°C for 1 hr. The results of Raman spectroscopy revealed that all the specimens exhibited an anatase titania layer due to the surface modification. The SEM analysis (Figure 1) showed a porous layer in the micrometer range for Ti and Ti-6Al-4V alloy. But Ti-15Mo alloy exhibited well networked porous structure in the nanometer scale.







Figure 1 shows the SEM images of hydrogen peroxide and heat treated (a) Ti, (b) Ti-6Al-4V and (c) Ti-15Mo alloy

The in vitro characterisation of surface modified specimens were carried out by immersing in simulated body fluid solution for 1 week. The results of FTIR spectra showed peaks at 575 cm⁻¹ and 1006 cm⁻¹ corresponding to phosphate and carbonate ions that has been incorporated in the apatite layer. The formation of apatite layer was further confirmed using SEM-EDAX analysis

Further, the corrosion behaviour of surface modified specimens in simulated body fluid solution was studied using open circuit potential, potentiodynamic polarisation and electrochemical impedance spectroscopy. The results have proved that e surface modified titanium and its alloys found to improve their corrosion properties and induced apatite deposition within a short period of time.

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P-029

Water Uptake and Diffusion of Chloride Ions in Seawater-Epoxy Coating-Steel Systems

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The barrier properties and the metal/coating interface for three commercial epoxy primer coatings on carbon steel substrates in seawater have been investigated by electrochemical impedance spectroscopy (EIS) technique. The absorption of water in the coatings during 23-week exposure in natural sea water has been analyzed based on data interpretation of EIS measurements, open-circuit potential (OCP) shift and surface appearance.

Water uptake has been determined by capacitance method using Brasher-Kingsbury equation and barrier properties of the coatings have been evaluated. Kinetics of water and ion penetration through primer coatings has been discussed and some kinetic parameters have been determined. Two stages of the penetration process can be defined from the relationship between coating capacitance (C) and exposure time (τ). It was

found a linear dependence of lnC vs. $\sqrt{\tau}$ in the early stage of water penetration, from which the apparent diffusion coefficients of water through epoxy primer layers can be calculated. These values are fluctuated in the range of (2.18–2.69) x10⁻⁹ cm²/s. The diffusion of Cl⁻ ions is suggested to be taken place after water saturation and their diffusion coefficient in studied primer coated – low carbon steel systems have the order of 1.5×10^{-11} cm²/s.

White Bronze Plating as a Possible Substitute for Nickel in Decorative Chromium Plating.

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Industries that plate chromium onto nickel are looking for an alternative to the nickel layer. The chromium deposit is typically porous when plated to a thickness of 0.3 micrometers and as a result the plated nickel underneath is then exposed through the pores of the chromium deposit. This exposure to the nickel is the cause of nickel dermatitis, which affects around 10-15% of women and 1-2% of men. Recent publications have shown that nickel dermatitis is on the increase with mobile phone users because nickel/chromium coatings are used on the outer casings. Other industries, where the public are exposed to nickel/chromium coatings, have also found this to be a growing concern, for example the automotive industries electroplate the door handles and other interior parts with nickel/chromium. The driver and passengers of these vehicles will be exposed to the nickel/chromium parts and so the potential for an allergic reaction to the nickel is feasible.

Information on bronze plating was first published in 1842 by Ruolz, making it more than 150 years old. The formulation for bronze plating has not changed significantly over the years; today it is still formulated with cyanide. Research into cyanide free formulations has led to a number of patents being granted and many publications but without successful commercialisation. White bronze, also known as speculum, has an alloy composition of approximately 50% copper/tin and is white in appearance. Varying the percentage of copper and tin in the deposit allows different variations of colour. White bronze is widely used in the jewellery industry as a replacement for nickel, which was in turn used as a cheap alternative to silver.

Research at the University of Wolverhampton has shown that using white bronze under chromium can provide a similar appearance compared to nickel/chromium deposits. Using a colorimeter, the white bronze deposit is lighter and bluer than the bright nickel but when chromium is used as a topcoat the colour difference when using white bronze or nickel as an undercoat is not significantly different.

Linear polarisation technique can determine the corrosion current densities (Icorr) of different deposits. Laboratory results illustrate that white bronze has a lower corrosion current density compared to bright nickel; chromium on top of either nickel or white bronze has no significant difference in Icorr.

Corrosion testing using a 5% sodium chloride neutral salt spray solution showed the corrosion resistance of the nickel/chromium deposit was better than white bronze/chromium. The comparison between nickel and white bronze showed that the nickel did not have any corrosion sites after 24 hours but did exhibit some discolouration, whilst the white bronze did have the start of corrosion sites.

In conclusion, white bronze could not directly replace nickel where maximum corrosion protection was essential; it could however replace nickel where the main requirement was an attractive appearance using a chromium topcoat.

Effect of additive on etching pit behavior of aluminum under AC etching process

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The aluminum electrolytic capacitor provides a unique value in high-energy storage and low device impedance. Fine surface etching accomplished mainly by AC electrolysis is generally used for low voltage foil. It is necessary to increase the surface area since the wider surface of the aluminum foil electrochemically was very important. The effect of various factors at AC electrolyte etching for pure aluminum foil was investigated. A study has been made of the fabrication conditions for etching cube texture of high purity aluminum foil and of electrochemical etching of the aluminum foil. In case of sulfuric acid, the etch-pits are growing into inner-layer of the aluminum foils as the sulfuric acid is made use of the corrosion inhibitor. The capacitance of the etched aluminum foil used in electrolytic capacitors is determined by its surface area. The methods of etching are selected according to the forming voltages. It is important for determining the etching mechanism to investigate the nucleation processes of pit formation. Many studies have also discussed the growth of pits using high-purity aluminum foils during AC etching in hot HCl solutions with respect to the effect of electrolytic conditions on the pit shape, morphology of the early stages of the pitting corrosion, the tunnel pit growth rate and the effect of impurities on the AC etching behavior. The principal purpose of the present work was to observe the morphologies of pit nucleation and to study the relation between changes in their capacitance during the early stage of AC etching and pit structures by using various conditions, such as electrolyte, current density, frequency and additive as ethylene glycol and AlCl₃. In general, hydrochloric acid is used for the etching solution, but because of its high corrosiveness the size and distribution of etch pits are not uniform with the low density. In this study, we investigated the effect of the additives of H_2SO_4 , AlCl₃ and ethylene glycol to HCl solution on the etching behaviors, and the relationship between etched morphologies. We have investigated the additive effect of high-purity aluminum foil on the performance during AC etching for aluminum electrolytic capacitor. The comparison of the surface-related capacitances of well characterized samples with the amount of additive suggests a strong contribution of etch pit density to electrolytic etching in the etchant solution. And the addition of AlCl₃ to the etching solution of HCl has an influence on the distribution of etching behavior in the wave form for the aluminum foil which causes the increase in the wave form.

Investigation of the polymer/oxide/metal interface stability with an in-situ Scanning Kelvin Probe Blister Test

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The incorporation of water and hydrated ions at polymer/oxide/metal interphases leads to a reduction of adhesion forces and an acceleration of corrosion reactions. The mechanisms of interfacial ion transport processes were and are currently under investigation. But studies usually neglect that polymer coated components often undergo mechanic deformations during usage. This distinctly degrades the interface and affects the prediction of its lifetime. Therefore it was intended to explore the interaction of the atmospheric humidity with a variation of the mechanic and electrochemical 'load' at the interface. For this purpose the Scanning Kelvin Probe Blister Test (SKP-BT) was developed. Its setup consists of a partially freestanding adhesive film above a substrate hole that can be pressurised from the backside. The SKP is height regulated and simultaneously detects the topography of the polymer surface and the polymer/substrate interface potential. The metal/liquid interface near the substrate hole can be also specifically polarised with a reference and counter electrode that are immersed into the electrolyte solution.

We observed that the electrochemical degradation precedes a macroscopic mechanic de-adhesion process even at high electrolyte pressures at the interface. High pressures generally accelerated the kinetics of cathodic delamination, but an increased polarization was even more effective. The relative humidity of the surrounding atmosphere strongly influenced the progress of corrosive de-adhesion during both the variation of the hydrostatic electrolyte pressure and a polarization of the defect zone. Polarization seemed to result in a self-inhibition of the electrode kinetics at a low atmospheric humidity.

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Formation and corrosion behavior of artificial pit of 2024 aluminum alloy with PRM

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It is well known that corrosion morphology in chloride containing environments of aluminum alloys is pitting corrosion. The aspect ratio of pit is very important role in propagation or growth of pitting corrosion. To clarify the effect of pit aspect ratio on the behavior of pitting corrosion, PRM (Photon Rupture Method; focused pulsed Nd-YAG-laser irradiation to remove materials from substrate) was applied. The purposes of this study are to investigate the effect of aspect ratio on dissolution behavior of the artificial pits formed in 2024 aluminum alloy by using modified laser activation technique and to develop higher aspect ratio pit formation technique.

A porous type anodic oxide film formed 2024 Aluminum alloy sheets were used for specimen. To form aspect ratio controlled artificial pit on the specimens, the specimens were irradiated by focused Nd-YAG laser beam at different time, t_i , in 0.5 kmolm⁻³ H₃BO₃/0.05 kmolm⁻³ Na₂B₄O₇ with and 1 molm⁻³ NaCl. Shape of formed artificial pit was investigated by confocal scanning laser microscope and X-ray Computed Tomography (X-ray CT). After formed artificial pit, rest potential was measured.

Figure 1 shows example of X-ray CT cross sectional image of artificial pit (aspect ratio is about 1.8) formed specimen. The depth was changed by laser beam irradiation time. These results show that PRM makes it possible to form aspect ratio controlled artificial micro-pit in solution.

Figure 2 shows change rest potential of formed artificial micro-pit, $t_i = 1s$ and 120S. During laser irradiation, rest potential keeps at low value about - 1000 mV. After laser beam irradiation, rest potential of both specimens return to original value of before laser irradiation. The returning rate is change with t_i .



Fig. 1 X-ray CT cross sectional image

Fig. 2 Changes in rest potential of formed pit

Electrochemical behaviors of AZ31 and AZ91 Mg alloys in alkaline and chloride solutions

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Magnesium alloys have always been attractive to designers due to their low density. The attention towards the using of magnesium alloys has been increased recently due to do the ever increasing demand to reduce the fuel consumption and pollution. AZ91 magnesium alloy is the most widely used among magnesium die-casting alloys is AZ91. On the other hand, AZ31 magnesium alloy is commonly used in stamping processes for the obtaining of components for aerospace, automotive and electronic industries.

In the present work, a comparative fundamental study has been carried out on AZ31 and AZ91 magnesium alloys in order to understand the electrochemical behavior in various solutions. The open circuit potential (OCP) was measured in 1 M NaOH and 3.5 mass% NaCl solutions. The passivation film on AZ91 seems to be compact and the corrosion product's film doesn't cover the entire surface after immersion for 5 hrs in 3.5 % NaCl solution.

The specimens were anodized at a constant potential of 3 V for 30 minutes at 298 K. The anti-corrosion behaviors of both alloys were evaluated using the anodic polarization curves and the electrochemical impedance spectroscopy (EIS). The anti-corrosion property of AZ91 anodic film is better than AZ31 anodic film due to the formation of MgO and $Mg_{17}Al_{12}$ and increasing of the anodic film thickness.

The passivation film on AZ91 seems to be compact and the corrosion product's film doesn't cover the entire surface after immersion for 5 hrs in 3.5 % NaCl solution.

Effect of operation conditions during plating on electrochemical behavior and morphology of chromium films

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Chromium plating based on trivalent electrolytes is an alternative for the major problems associated with hexavalent traditional plating. In this work chromium films were obtained to different chromium concentration, pH and temperature during plating, the experiments were carried in a chloride based bath to (10, 20 and 30 g/L as Cr^{+3}), three pH (2.0, 3.0 and 4.0) and three temperature (25, 32, 40 °C). It was observed to different morphology and different corrosion resistance after potentiodynamic and EIS tests on NaCl 3%, for corrosion tests a conventional tree electrode cell with a SCE electrode was employed. The visual quality of films were affected mainly by the pH and concentration, also the morphology was modified by this finding a micro cracking pattern on films obtained to high pH values independently of the temperature.







Figure 2. Potentiodynamic curves in NaCl 3% for chromium films obtained to different operation conditions, v=0,2 mV/s.

Application of Nanostructured Materials as Host Structures for Corrosion Inhibitors

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The most common strategy to protect metallic structures against corrosion is based upon the application of organic coatings loaded with corrosion inhibitors. However, two major drawbacks are associated with this methodology: the spontaneous leaching of inhibitors, and the detrimental interaction between coating matrix and active species [1]. One way of extending both passive and active protection over time is to use inert nanomaterials capable of storing the inhibiting species for an indeterminate period of time, releasing them only certain conditions in the surroundings are met (pH, presence of aggressive ions or electrochemical potential [2]).

In this work, we report the development of different types of nanocontainers, their loading with corrosion inhibitors and subsequent incorporation into coating

formulations. Structural, compositional morphological studies of and the nanocontainers (Figure 1), as well as release studies of the active species using and chromatographic spectroscopic techniques will be presented [3]. The anticorrosion activity of the resulting systems is here assessed by Electrochemical Impedance Spectroscopy (EIS), and the Scanning Vibrating Electrode Technique (SVET) [4].

The results will show that the coating performances depend on the type of inhibitor and release mechanisms associated with the host structures, and



Figure 1: TEM image of Layered Double Hydroxide nanocontainers

also that the self-healing of micro-confined defects can be achieved by careful selection of active-guest and inert-host structures.

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In-situ Monitoring Undercoating Corrosion Damage of Al Thin Film by Direct Optical Interrogation (DOI)

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A novel approach (Direct Optical Interrogation, DOI) is presented for detecting and studying the localized corrosion of undercoating corrosion processes. This involves studying the growth of pits in a deposited 800nm Al thick film, with a commercial coating on top, on a transparent inert substrate in chloride solution (0.5 M NaCl + 0.5 M HCl). The pitting corrosion activity is monitored by an inverted stereo optical microscope, thus directly observing the corrosion underneath organic coatings and producing a quantitative determination of undercoating corrosion kinetics. Corrosion initiates with the development of pits that penetrate the film near an artificial defect. The defect then grows outward in the lateral direction, followed by the onset of large bubbles during the corrosion process. After fifteen hours, the pits near the defect stop growing. At the end of the process, smaller pits start to initiate and propagate. By integrating the electrochemical experiments (EIS) with the optical image analyzer, the undercoating corrosion damage can be estimated.

Electrochemical characterization of Ce (La)-based coatings on commercial AA6061 aluminum alloy.

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Ce (La)-based coatings were synthesized by immersion process at different concentrations, immersion times and temperatures, in order to study the improvement of the anticorrosive properties of commercial AA6061 aluminum alloy. The coatings were characterized by X-ray diffraction (XRD), optical microscopy (OM), open circuit potential (OCP), polarization resistance (Rp), Tafel plots and electrochemical impedance spectroscopy (EIS) using an aggressive medium of NaCl solution (3.5 wt%). AA6061 aluminum alloy discs (diameter: 0.025 m, thickness: 0.02 m) were polished up to 2000 grade SiC paper, cleaned with soapy solution and rinse with deionized water. 0.01, 0.1, 0.5 and 1.0 gL⁻¹ cerium nitrate and lanthanum nitrate solutions were prepared. After cleaning the AA6061 disc samples, they were immersed in the cerium nitrate or lanthanum nitrate solutions during 60, 600 and 1800 minutes at 50, 70 and 90 °C. According to the electrochemical results, the best coatings were those of lanthanum (Figure 1 a-d).



Figure 1. Nyquist plots of La solution at 90 °C (a) 0.01 gL^{-1} (b) 0.1 gL^{-1} (c) 0.5 gL^{-1} (d) 1.0 gL^{-1}

Effect of Metal Glass Coating on the Electrochemical and Corrosion Behavior of 316L Stainless Steel Bipolar Plate for Fuel Cell Application

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The electrochemical behavior of 316L stainless steel (SS) bi-polar plate substrate, with or without metallic coating, in simulated fuel cell environment was investigated. Two coatings, namely (1) single layer of ZrCuAlNi amorphous metal (NG) and (2) nano-multilayered pure metals (NMZr), respectively, were investigated in this study. The polarization behaviors of these two coated specimens were evaluated in 1M H_2SO_4 solution by conducting potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests. The experimental results showed that the nano-multilayered coating had a high polarization resistance than the ZrCuAlNi amorphous coating. The difference in polarization resistance was determined by the chemical composition of the passive films formed on different coated electrodes.



Fig. 1 Nyquist plots of 316L SS and those with NG and NMZr coatings, in 1 M $\rm H_2SO_4$ solution.

Monitoring of Some New Scaffolds Behavior in Simulated Body Fluid

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The interactions, for long term of some scaffolds with 3D structure formed by hydroxyapatite (HA), β -tricalcium phosphate (β -TCP) and hydroxyapatite+ β -tricalcium phosphate (HA+ β -TCP) in simulated body fluid (SBF) were studied by the monitoring of their behavior (variation of their weights and structures) and by the monitoring of the changes of SBF pH values and composition, for to detect the two simultaneous processes that take place: deposition of calcium and phosphorous ions coupled with the slow, progressive, gradual dissolution of the materials.

SBF had the following composition (g/L): NaCl-7.99; KCl-0.224; NaHCO₃-0.35; K₂HPO₄.3H₂O-0.228; MgCl₂.6H₂O-0.305; CaCl₂-0.278; Na₂SO₄-0.071.

The induced coupled plasma-optical electron microscopy, ICP-OEP was used for the determination of long term (3600 exposure hours) variations of calcium and phosphorous ion contents from SBF, for to monitory their deposition on the scaffold surfaces. The scanning electron microscopy, SEM was applied for to study the morpho-structural, long term changes (3600 hours till present) of the materials. Also, the scaffold weights were periodically verified and the variations of the simulated body fluid pH values were monitored for long term.

The concentration of the calcium and phosphorous ions from SBF solution had decreased in the first 200 immersion hours as result of their deposition on the sample surfaces; after that, the concentrations of these ions had approximately remained constantly, following the fact that, the those two processes of deposition and dissolution were compensated; consequently, the bone formation is coupled with the scaffold resorption.

The scaffold weight variations revealed the fact that, after 170 immersion hours, simultaneously with the deposition of the calcium and phosphorous ions take place the slow dissolution (resorption) process.

The pH values of SBF solution had increased at beginning due to the dissolution of the soluble phases from these materials and then had maintained to constant values, because of the ion deposition process that exceeds the dissolution process, therefore, the material bioactivity increased in time.

The morpho-structural studies had confirmed the above observations: after 170 immersion hours in SBF appeared deposition of flakes and aggregates of flakes specially at the grain junctions, roughness increased and the porosity decreased; after 360 immersion hours, on the HA surface were observed spider-web like net connecting long thin filaments; the surface of β -TCP scaffold was covered with aggregates of deposited flakes and the nanoparticle aggregates are ubiquitous, covering areas of hundred of microns; the surface of HA+ β -TCP scaffold was covered with a layer of acicular grains.

Passivity Behavior and Long Term Stability of a New Non-toxic Implant Alloy

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A new alloy that contains only non-toxic elements, Ti-10Zr-5Ta-5Nb was obtained. Anticorrosive resistance of this new alloy was studied in simulated physiological fluids, Ringer solution, in extreme functional conditions, namely acidic, neutral and alkaline pH. Acidic pH appears after surgery (because the hydrogen ions concentration increases in the traumatic tissues) and by the hydrolysis in time of the protective oxides; alkaline pH forms rarely, in the illness periods of the human body.

Ti-10Zr-5Ta-5Nb alloy was obtained by vacuum melting with the composition: Zr– 9.12; Nb–0.9; Ta –4.16; Fe–0.036; O₂–0.195; N₂–0.004; H₂-0.0016; Ti – up to the balance.

All measurements were carried out in Ringer solution of pH = 2.33 (obtained by HCl addition), pH = 7.1 (normal pH) and pH = 9.12 (obtained by KOH addition). Solution composition (g/L) is: NaCl-6.8; KCl-0.4; CaCl₂-0.2; MgSO₄.7H₂O-0.2048; NaH₂PO₄.H₂O-0.1438; NaHCO₃-1.1; glucose-1. Temperature was kept at $37^{0}\pm1^{0}$ C.

The electrochemical techniques of potentiodynamic and linear polarization were used. Cyclic potentiodynamic measurements were applied for to determine the main electrochemical parameters: E_{corr} -corrosion potential, like the zero current potential; E_p -passivation potential; E_{cp} -complete passivation potential; ΔE_p -passive potential range; i_p -passive current density. Linear polarization measurements (Tafel curves) were carried out and the corrosion current densities i_{corr} and rates V_{corr} were obtained. The open circuit potentials were monitored in time (5000 exposure hours) and with pH values. The possible open circuit potential gradients that could appear due to the non-uniformity of Ringer solution pH were determined.

In Ringer solution of acid pH < 3, corrosion rate shows behaviour in the "Stable" category and the main electrochemical parameters characterize the alloy as being passive and resistant. In Ringer solution of normal pH = 7.1, the Ti-10Zr-5Ta-5Nb is "Very Stable", is self-passivated and all electrochemical parameters have favourable values for a good stability and resistance to corrosion. In Ringer solution of alkaline pH > 9, the Ti-10Zr-5Ta-5Nb alloy also presented a good resistance to corrosion and a stable passive state.

The open circuit potentials for Ti-10Zr-5Ta-5Nb alloy are more electropositive than of Ti, showing that the passive films formed on the alloy surface are non-reactive and more resistant than those formed on Ti surface.

The values of open circuit potential gradients for Ti and Ti-10Zr-5Ta-5Nb alloy are very low and cannot generate galvanic or local corrosion, even in the extreme case of a very large pH difference of 2.33 and 9.12.

All electrochemical parameters are better for the Ti-10Zr-5Ta-5Nb alloy than for Ti, proving the beneficial effects of the alloying elements.

Inhibition Mechanism and Anticorrosive Behaviour of Calcium Exchanged Silica Pigment

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Organic coatings with hexavalent chromium compounds (chromates) as inhibitive pigments have been widely used. However, its high toxicity and carcinogenic effects are forcing the development of effective chromate-free organic coatings. Nowadays ion-exchangable pigments (hydrotalcites, bentonites and silicas) are an attractive alternative that is being explored. In this study the possibilities offered by a calcium exchanged silica pigment (Shieldex®) are analyzed, to know in depth the inhibition mechanism and to assess the anticorrosive behaviour of organic coatings formulated with this pigments. Organic coatings formulated with Shieldex® pigment were applied on carbon steel and aluminum specimens. Traditional zinc chromate pigment was also included for comparative purposes.

Potentiodynamic polarization measurements were carried out on carbon steel and aluminium using the pigment aqueous extracts as electrolyte. Metal surface characterization was carried out by XPS. EIS measurements were also obtained to study the anticorrosive behaviour of the coating systems.

Experimental results showed a cathodic inhibition of both metals immersed in pigment aqueous extracts and the formation of a protective film. A good anticorrosive behaviour of the coating system was also observed.

Keywords: Calcium exchanged silica, chromate-free coatings, corrosion inhibition, organic coatings, ion-exchangable pigments.

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Corrosive Performance of Ti/SnO₂+Sb₂O₄/CF/PbO₂ Acid-Proof Anode

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There are few appropriate anodic materials in industry due to the strong corrosiveness and oxidation in acid solution, some noble metals are suitable but expensive, and some other non-noble metals anode are still noticed by many researches and the test are still in progress in laboratory^[1]. The Carbon fiber(CE) has the property of acid resistant and its conductivity is high, hence we introduced the carbon fiber into Ti/SnO₂+Sb₂O₄/PbO₂ anode, using it as intermediate layer formed a kind of new anode of Ti/SnO₂+Sb₂O₄/CF/PbO₂ and hope this anode has a high anti-corrosion, service life and good properties for oxide reactions.

Electrochemical experiments

The Ti/SnO₂+Sb₂O₄/CF/PbO₂ electrode was prepared by the combination technology of thermal decomposition and electro-deposition, the detailed preparation steps see Refs^[2]. The morphology and crystal phase of the electrode were characterized by means of SEM and XRD. The anticipated service life of the anode was inspected by the way of accelerated life tests^[2].

Results and Conclusion

The service life of Ti/SnO₂+Sb₂O₄/CF/PbO₂ electrode was 130h in 1.0mol/L H₂SO₄ at 4A/cm² according to the method of Refs^[3]. The intermediate layer of SnO₂+ Sb₂O₄+CF can reduce the product of TiO₂ insulator because it can stop the diffusion of oxygen effectively. If some TiO₂ was produced, they can form continuous solid solution. because the crystal lattice parameters of SnO₂, PbO₂ and TiO₂ are very close. Another reason why the electrode lifetime is so long is the conductance of SnO₂+Sb₂O₄/CF is well. When Sb₂O₃ and Sb₂O₅ were doped into SnO₂ the conductivity of SnO₂ was increased because of the production of oxygen vacancy, and defect Sb_{sn}.

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Comparison of Semiconductor Properties for Pretreatments on Steel: Progress Toward Characterization and Performance Prediction for Zirconium Nanoscale Coatings (Zr-nsC)

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There is an increasing commercial trend to replace traditional zinc phosphate metal pretreatments with zirconium nanoscale coatings (Zr-nsC). Zr-nsC offer a more environmentally conscious and sustainable approach for industrial scale metal finishing by eliminating production of heavy metal phosphate sludge and the cost for waste treatment of this sludge. Zr-nsC also offer additional cost reduction due to the energy savings made possible by room temperature deposition. These benefits encouraged the widespread adoption of Zr-nsC in metal finishing operations. However, the unique properties that have made Zr-nsC so practical have simultaneously made characterization very difficult.

The scanning electron microscope (SEM) traditionally used to assess the quality of a microcrystalline zinc phosphate is not equally useful for Zr-nsC. The SEM reveals much less detail for Zr-nsC due to the thin and amorphous nature. To develop techniques for characterizing Zr-nsC, a simultaneous effort was necessary to establish structure-property relationships. This needed to be done for each new formula investigated in the context of each newly explored analysis type.

A combination of Mott-Schottky analysis (MS) and Potentiostatic Electrochemical Impedance Spectroscopy (EIS) was used to develop comparative methods for understanding the quality of various pretreatments based on changes in semiconductor type and chemical composition (i.e. phosphate vs. oxyhydroxide). The use of such techniques has been known academically for many years and even recently suggested for studying delamination of organic coatings.^{1, 2, 3} However, the application of these techniques to industrial Zr-nsC has not been reported. Here we report on progress towards characterization of the basic electronic and barrier properties of Zr-nsC in comparison to zinc phosphate. With continued progress a comprehensive set of tools could be available for predicting relative performance of metal pretreatments to resist corrosion and assist in adhesion of organic coatings.

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