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CURRENT ACTIVITIES and PRESENTATIONS

AFFILIATE MEMBERS

ABSTRACT of PUBLICATIONS

CURRENT ACTIVITIES and PRESENTATIONS

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R. Ogawa, H. Takahashi, S. Mizukami, T. Yoshioka

Our research activities are concerned with molten salts or ionic liquids electrolysis, water electrolysis, surface sciences about metal surface, and fuel cell.

Current topics on research are in the following:

(1) Electrorefining of Na for recycling of used Na-S secondary batteries

To develop electrorefining process of metallic Na from the used Na-S battery. There is no electrorefining process of sodium in the industrial scale. We were investigated NaFSI-TEATFSI ionic liquid as candidate of the electrolytic melt. In the electrorefining experiment for more than 20 hours, 99.98 % pure Na was obtained from simulated Na in used Na-S battery.

(2) Electrodeposition of Al-Zr alloys in chloride molten salt

To improve the corrosion resistance of Al in chloride solutions, electrodeposition of Al-Zr alloys of various compositions was carried out at 448 K by constant potential control in $AlCl_3$-NaCl-KCl molten salt containing $ZrCl_4$. The electrodeposition was performed by constant potential electrolysis from -1.4 to -1.6 V.

(3) Development of Al-Cl_2 cell in ionic liquid

To develop an aluminum-chlorine cell, an electrochemical cell consisting of an aluminum anode and a graphite cathode was developed and evaluated in EMIC-$AlCl_3$ ionic liquid.

The relationship between current density and cell voltage in the cell showed an almost linear relation. The output characteristics of the cell depend on the configuration of the graphite cathode, the current density with a circular cone type cathode at 0.5 V was about 40 % better than that of a cylindrical type graphite cathode.

(4) In-situ observation of electrochemical interfacial phenomena by Video-AFM

We have developed the atomic force microscopy with fast scanning rate (Vide-AFM) and in-situly observed the electrochemical nucleation/dissolution. At the present, Cu electrodeposition/dissolution on HOPG substrate has been investigated in aqueous sulfuric acid solution. We will analyze the growth or dissolution late from one nuclei.

(5) Deuterium isotope separate

We are exploring the possibility of hydrogen isotope separation by using several types of fuel cells and alkaline water splitting. The separation factor of D/H during polymer electrolyte and alkaline fuel cells is measured by quadrupole mass spectroscopy (Q-mass). We try to build novel separation system where the electrolysis is combined with the fuel cells.

(6) NIR study for Nafion membrane below freezing temperature

We in-situly apply near infrared spectroscopy (NIR) for Nafion membrane below freezing temperature. Simultaneously, we carry out the impedance measurement in order to research the conductivity mechanism of the polymer. We find the water molecules confined in Nafion membrane take supercooling state down to -140℃.

Other Activities

Prof. Ueda was invited in Workshop on the Electrochemistry of Electroactive Materials 2015(WEEM 2015), and present paper entitled by "Corrosion protection of mild steel by conductive bilayered polypyrrole film", Bad Herrenalb, Germany, May 31-June 5, 2015. Prof. Ueda attended 228th ECS meeting, and present paper entitled by "Electrodepotision of Metallic Silicon in P13TFSI Ionic Liquids Containing $SiCl_4$", Phoenix, USA, October11-15, 2015.

Presentations

Investigation of multi-layer electroplating using ionic liquids; S. Honda, H. Matsushima, M. Ueda, A. Ispas and A. Bund: Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 27- 28, 2015.

Kinetic discussion of isotope effect in hydrogen electrode reaction; S. Shibuya, H. Matsushima, M. Ueda: Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 27- 28, 2015.

Impedance and NIR measurement of Nafion membrane below freezing temperature; Y. Kouno, H. Matsushima, T. Ohtsuka, M. Ueda: Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 27- 28, 2015.

Behavior of Ca and K from metallic Na in Na electrorefining using NaFSI-TEATFSI ionic liquid; Y. Yasui, H. Matsushima, T. Ohtsuka, M. Ueda: The winter joint meeting of the Hokkaido secs. of Jpn. Inst. Metals and iron and steel Inst. Jpn., Hokkaido University, Sapporo, January 29-30, 2015.

Electrodeposition of Al on porous Ni in EMIC-$AlCl_3$ ionic liquids; R. Nakanishi, H. Matsushima, A. Hyono, M. Ueda: The winter joint meeting of the Hokkaido secs. of Jpn. Inst. Metals and iron and steel Inst. Jpn., Hokkaido University, Sapporo, January 29-30, 2015.

Electrodeposition of Al-Ta alloys in $AlCl_3$-NaCl-KCl molten salts containing $TaCl_5$; K. Sato, H. Matsushima, M. Ueda: The winter joint meeting of the Hokkaido secs. of Jpn. Inst. Metals and iron and steel Inst. Jpn., Hokkaido University, Sapporo, January 29-30, 2015.

Corrosion protection of mild steel by conductive bilayered polypyrrole film; M. Ueda, M. Sasaki, T. Ohtsuka: Workshop on the Electrochemistry of Electroactive

Materials 2015(WEEM 2015), Bad Herrenalb, Germany, May 31-June 5, 2015.

A NIR study of conductive mechanism of Nafion membrane below freezing temperature; Y. Kohno, H. Matsushima, T. Ohtsuka, M. Ueda: The summer joint meeting of the Hokkaido secs. of Jpn. Inst. Metals and iron and steel Inst. Jpn., Muroran institute of technology, Muroran, July 17, 2015.

Electrodeposition of Al-Ta alloys in low temperature chloride molten salts containing Ta ions; K. Sato, H. Matsushima, M. Ueda: Summer Meeting of Hokkaido branch of Japan Chemical Society, Hakodate campus of Hokkaido Educational University, Hakodate, July 18, 2015.

A measurement of deuterium separation factor by PEFC; S. Shibuya, Matsushima, M. Ueda: Fall meeting of ECSJ 2014, Saitama Institute of Technology University, Fukaya, September 11-12, 2015.

Electrochemical interfacial phenomena at gas evolving electrode; H. Matsushima, M. Ueda: 6th international symposium on physical science in space, Doshisha University, Kyoto, September 14-18, 2015.

Analysis of bright surface of Al electroplating formed from ionic liquids; M. Ueda, C. Namekata, H. Matsushima: 130th annual meeting of Surf. Finish. Soc. Jpn, Shinsyu University, Nagano, September 22-23, 2015.

Kinetic isotope effect on hydrogen evolution and oxidation reactions; H. Matsushima, S. Shibuya, R. Ogawa, M. Ueda: 66th annual meeting of ISE 2015, Taipei, Taiwan, October 4-9, 2015.

A New Challenge for Hydrogen Isotope Electrolytic Separation System Combined with Fuel Cell; H. Matsushima, S. Shibuya, R. Ogawa, M. Ueda: 228th meeting of ECS 2015, Phoenix, USA, October 11-15, 2015.

Electrodepotision of Metallic Silicon in P13TFSI Ionic Liquids Containing $SiCl_4$; A. Tsuruta, H. Matsushima, M. Ueda, T. Fujii, H. Date: 228th ECS Meeting, Phoenix, USA, October11-15, 2015.

A NIR study of conductive polymer membrane below freezing temperature; Y. Kohno, H. Matsushima, T. Ohtsuka, M. Ueda: 31st NIR forum 2015, Tsukuba University, Tsukuba, November 25-27, 2015.

Electrodepotision of Silicon film in LiCl-KCl chloride molten salt; A. Tsuruta, H. Matsushima, M. Ueda, T. Fujii, H. Date; 47th symposium on molten salt chemistry and technology, Kobe University, Kobe, October 28-29, 2015.

Output characteristics of Al-Cl_2 fuel cell in graphite cathodes with different density; S. Honda, H. Matsushima, M. Ueda: 47th symposium on molten salt chemistry and technology, Kobe University, Kobe, October 28-29, 2015.

Kinetic study of hydrogen isotope effect on hydrogen electrode reactions; S. Shibuya, H. Matsushima, M. Ueda: The international chemical congress of pacific basin society 2015, Honolulu, USA, December 15-20, 2015.

Facilities and Capabilities

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light and null-method ellipsometer for multiple-angle-of-incidence measurement.

Raman Scattering Spectrometer: Bunko Keiki, single type of spectrometer equipped by high sensitive CCD.

FT-IR Spectrometer: JASCO FT/IR 4200 equipped with MCT detector, IR-RAS apparatus and IR microscopy system.

QCM system for in-situ gravimetry of surface layer on metals.

Electrochemical AC Impedance: NF Circuit Design 5020 FRA and 5095 FRA equipped with a specially designed potentiostat.

Electrochemical AC Impedance: Solartron 1260

ICP atomic emission spectrometer: Thermo i-CAP 6000.

Carl Fischer moisture measuring system: Metrohm 852 titrando.

Evaporator: Eyela SB1100.
Electrochemistry apparatuses.

Optical Microscopy.

Electrochemical Corrosion Rate Monitor System.

Molten salt ion-exchange apparatus for glass.

Luminescence apparatus for thin surface layer equipped with He-Cd UV laser.

Video scanning rate Atomic Force Microscopy (Video-AFM).

Quadrupole Mass Spectroscopy (Q-Mass): ULVAC Quless CGM-052 and HGM-202.

Rotating Disc Electrode (RDE) system.

Near Infrared Spectrometer: Ocean optics NIR256-2.1

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A. Kasuga, Y. Kunii, T. Yamaguchi,

In October Assistant Professor Etsushi Tsuji left our laboratory and promoted lecturer at Graduate School of Engineering, Tottori University. Prof. Soo-Gil Park, Chungbuk National University, stayed in our laboratory as a Visiting Professor from July 1st till the end of November. Ms. Su-Bin Yang from Korean National University of Transportation and Mr. Jun-Hong Lee from Chungbuk National University stayed in our laboratory as an internship student in July. Mr. Andrea Zaffora from Palermo University joined our laboratory from November 1st as an internship student for three months.

The research activities of the laboratory are directed towards the development of advanced oxide films and nanomaterials utilizing anodizing process, sol-gel process and PVD for possible applications including novel fuel cells, air batteries, photovoltaic cells, corrosion protection, self-cleaning surfaces and capacitors. We are also interested in surface analytical techniques with nanoscale resolution for a better understanding of the interfacial phenomena of metal and semiconductor electrodes in relation to electrochemical devices for energy storage and conversion, corrosion, passivation and surface finishing.

Current topics on research are in the following:

(1) Formation of self-ordered nanoporous nanotubular anodic films on iron and iron-base alloys

We successfully fabricated self-ordered nanoporous and nanotubular anodic films on iron and stainless steels in fluoride-containing ethylene glycol electrolytes. Critical factors controlling the composition and morphology of the anodic films were investigated in detail. Further, we succeeded to fabricate corrosion-protection composite coatings consisting of a polypyrrole conducting polymer layer and a porous anodic iron oxide layer. The composite coating showed highly improved corrosion protectin and adhesion to iron substrate in comparison with a single polypyrrole layer.

(2) Tailoring of mesoporous anodic TiO_2 films in novel hot phosphate-glycerol electrolytes

Recently, we have found that phosphate-glycerol solution at elevated temperature is a new electrolyte to form self-organized porous anodic films on various valve metals. Using this novel electrolyte, we obtained mesoporous anatase films without heat treatment. Such films will be suitable for various applications.

(3) Fabrication of superhydrophobic and superoleophobic surfaces

One of the important factors to control the surface wettability of solid materials is surface geometry. Hierarchical porous surface morphology is of particular importance to obtain superhydrophobic surfaces together with surface energy of solid materials. Further precise control of the surface geometry resulted in the formation of superoleophobic surfaces, on which oil droplets were readily rolled off. Utilizing porous anodic films, we developed hierarchical surfaces on aluminum and aluminum alloys and obtained superolephobic surfaces after coating with a fluoroalkyl monolayer, which had the lowest surface energy.

(4) Novel dielectric films formed by anodizing

One of the important practical applications of the anodic films on valve metals is dielectric in electrolytic capacitors. We have examined dielectric properties of the anodic films formed on a range of novel valve metal alloys. Detailed investigations on the significant enhancement of capacitance by forming nanocomposite anodic films, consisting of nanocrystalline tetragonal ZrO_2 phase and an amorphous matrix, have been conducted.

(5) Intermediate temperature fuel cells using a proton-conducting thin film electrolytes

Proton-conducting oxide thin films were fabricated by magnetron sputtering or sol-gel spin casting, and used for proton ceramic fuel cells (PCFCs). In the PCFCs we used a hydrogen-permeable metal anode, which acts as a blocking electrode for oxide ions. Research interest was also directed towards how to reduce the charge-transfer resistance at the proton-conducting electrolyte/cathode interface.

Other activities

Prof. H. Habazaki presented invited lectures entitled “Porous anodic oxide/polypyrrol composite coatings for corrosion protection of iron” at International Seminar on the Surface, Passivity and Corrosion of Metals, which was held on 18-21 January at Trondheim, Norway, “Corrosion protection of iron using porous anodic oxide/conducting polymer composite coatings”, at Faraday Discussion: Corrosion Chemistry, which was held on 13-15 April at Royal Society of Chemistry, London, “Characterization of Corrosion-resistant Aluminosilicate Coatings Prepared by Multiple Sol-Gel Spin Casting” at 17th Topical meeting of the International Society of Electrochemistry, which was held on 31 May-3 June at Saint-Malo’s Conference Center, Saint-Malo, France, and “Formation of Self-Organized Porous Anodic Films on Iron and Stainless Steels” at 228th ECS Meeting, which was held on 11-15 October at Phoenix Convention Center and the Hyatt Regency, Phoenix, Arizona, USA.

Presentations

“Photoelectrochemical Evidence of inhomogeneous Composition at nm length Scale of anodic Films on valve Metals Alloys”, F. Di Franco, A. Zaffora, M. Santamaria, H. Habazaki, F. Di Quarto, 17thTopical Meeting of the International Society of Electrochemistry, Saint-Malo’s Conference Center, Saint-Malo, France, May 31-June 3, 2015.

“Hydrogen Membranes Based on Group-IV Metal Nitrides”, Y. Aoki, C. Kura, E. Tsuji and H. Habazaki, 20th Int. Conf. Solid State Ionics, Keystone Resort & Conference Center, Keystone, USA, June 14-19, 2015.

“Hydrogen Permeability of TiNx Thin Films Prepared by RF Reactive Sputtering”, C. Kura, Y. Aoki, E. Tsuji, and H. Habazaki, 20th Int. Conf. Solid State Ionics, Keystone Resort & Conference Center, Keystone, USA, June 14-19, 2015.

“The Effect of Electrolyte Composition on Anodizing of Ti in the Hot Alkaline Glycerol Electrolyte”, Y. Okazaki, E. Tsuji, Y. Aoki, H. Habazaki, The 8th NagoyaUniv.-Tsinghua Univ.-Toyota Motar Corp.-Hokkaido Univ.-Xinjiang Normal Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st Century-, Xinjiang Normal University, Urumqi, China, August 8-11, 2015.

“Morphology Control of Anodic Iron Oxide Films and Their Application to ORR and OER Electrodes”, R. Tomizawa, E. Tsuji, Y. Aoki, H. Habazaki, The 8th NagoyaUniv.-Tsinghua Univ.-Toyota Motar Corp.-Hokkaido Univ.-Xinjiang Normal Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st Century-, Xinjiang Normal University, Urumqi, China, August 8-11, 2015.

“Oxygen Reduction Activity and Durability of Pt Electrocatalysts Supported on Platelet Carbon Nanofibers”, E. Tsuji, T. Yamasaki, Y. Aoki, K. Shimizu, S.G. Park, H. Habazaki, 66th Annual Meeting of International Society of Electrochemistry, Taipei International Convention Center, Taipei, October 4-9, 2015.

“Formation of Self-Organized Nanoporous and nanotubular Anodic Films on Iron”, K. Shahzad, E. Tsuji, Y. Aoki, S. Nagata, H. Habazaki, The 4th Joint Symposium Between Hokkaido University and Harbin Engineering, Hokkaido Univ., Sapporo, Japan Aug. 31-Sept. 2, 2015.

“Fabrication of Super-Liquid-Repellent Surfaces on Aluminum Mesh with Chemical Etching/Anodizing”, K. Nakayama, E. Tsuji, Y. Aoki, H. Habazaki, 66th Annual Meeting of International Society of Electrochemistry, Taipei International Convention Center, Taipei, October 4-9, 2015.

“Influence of Water Concentration on Growth Efficiency of Barrier-Type Anodic Film on Magnesium”, K. Shahzad, E. Tsuji, Y. Aoki, S. Nagata, H. Habazaki, 66th Annual Meeting of International Society of Electrochemistry, Taipei International Convention Center, Taipei, October 4-9, 2015.

“Catalytic Activity of Double-Perovskite Type $BaLnMn_2O_5$ for Oxygen Reduction Reaction Using in Rechargeable Zinc-Air Batteries”, E. Tsuji, T. Motohashi, Y. Aoki, H. Habazaki, 228th ECS Meeting, Phoenix Convention Center and the Hyatt Regency, Phoenix, Arizona, USA, October 11-15, 2015.

Facilities and Capabilities

DC and RF magnetron sputtering: Shimadzu SP-2C, suitable for preparation of various metallic thin films as well as oxide and nitride films.

FT-IR spectrometer: Jasco FT-IR350, equipped with DR and RAS attachments.

Ultramicrotomy: RMC MT-7 and PT-X, suitable for the preparation of electron transparent TEM sections.

AFM: SII SPA-400 system with conductive AFM mode as well as contact and tapping modes.

Impedance analyzer: Solartron 1260, measureable in the frequency range of 10 μHz to 32 MHz.

Contact angle meters: Kyowa Interface Science, Dropmaster system, to evaluate superhydrophobicity of solid surface.

Q-mass: Balzers Quadstar421 system for mass analysis of gases with mass number of less than 200.

Tribometer: CSM pin-on-disk tribometer for wear and friction characterization of coated material

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Prof. Ryosuke O. Suzuki merged as the professor of the laboratory of Eco-processing from Kyoto University on March 2006. He studies the non-ferrous metallurgy based on the molten salt electrolysis. His research activities are directed to design the economical and environment-friendly processes for materials production at high temperatures. The extraction metallurgy of the refractory metals such as Nb and Ta, and of valve metals such as Ti, V and Zr, serves many topics when the electrolysis of CaO in the molten $CaCl_2$ is applied. The electrolysis of CO_2 gas is one of the extreme cases in oxide decomposition.

Dr. Kikuchi joined as an associate professor from laboratory of interface microstructure analysis on May 2010, and he began to study the micro- and nano-structure fabrication by anodizing. Electroless calcium reduction of titanium, zirconium, neodymium, and iron oxides in calcium chloride molten salt at high temperature was also investigated for novel electronic device fabrication and recycling of these metals.

Dr. Natsui joined as an assistant professor from Tohoku University on April 2013. His research activities are directed to design the low-carbon ferrous metallurgy by using current numerical simulation technology such as discrete element method, its coupling to CFD, and particle based hydrodynamics. And he began to develop the rapid electro-reduction system by emulsified molten salt at high temperature.

Current topics on corrosion research are in the following:

(1) Molten salt electrolysis of $CaCl_2$

Reduction of the oxides of Ti, Nb and Ta are studied, when the CaO dissolved in the molten $CaCl_2$ is electrochemically decomposed to form metallic calcium. A low oxygen potential produces the metallic powders at the cathode. The reduced metallic powder is prepared directly from the oxides. The mechanism of this proposal is examined from the electrochemistry and thermodynamics. CO_2 gas reduction catches the current interests in the morphology of precipitated carbon particles.

(2) Nanostructure fabrication by anodizing

Anodic porous alumina has been widely investigated as a nanostructure template in various nano-applications. The nano-morphology of porous alumina is limited by the narrow range of electrolyte species used for anodizing. Therefore, the discovery of additional electrolytes would greatly expand the applicability of porous alumina. We have been working on anodizing in novel electrolytes, such as selenic and etidronic acid, for the formation of ordered porous alumina. Fabrication of high-density, highly ordered anodic alumina nanofibers was also demonstrated via two distinct anodizing processes: porous oxide formation in sulfuric acid and fibrous oxide formation in pyrophosphoric acid.

(3) Low-carbon ferrous metallurgical design

In a ferrous metallurgical process, multiphase flow plays an important role in increasing the efficiency by stirring liquid mechanically or by injecting a gas. Owing to the difficulty of direct observation in a high-temperature system or real furnace experiment, numerical analysis is useful and studied. We presents a new particle-based simulation scheme for gas-liquid flow. We improved the numerical stability, which is generally a problem with the particle method, and verified the model's accuracy for fundamental gas-liquid flow analysis. This scheme is also applicable to phenomena in an actual process that includes many dispersal phases.

Other activities

(4) Thermoelectric power generation

An optimization of the thermoelectric generation is mathematically designed for the highest output. This work links with energy harvesting to conduct the electrolysis. The utilization of solar energy is challenged using cheap materials such as water.

(5) Electro-reduction in suspended molten salt

The electrochemical reduction of metal oxides is an important process in active metal production. The OS process has revolutionized molten salt electrolysis; however, it still has diffusion and oxide rebuild-up issues. We attempted the electro-reduction in suspended molten salt with gas flow. This approach expects increasing reduction rate and eliminates some of these issues.

Prof. Suzuki made the plenary lecture on "Oxide reduction using electrolysis in $CaCl_2$-CaO or LiCl-Li_2O melt" at the 10th International Conference on Molten Salt Chemistry and Technology held at Northeastern University, Shenyang, China. The following foreign scientists visited this laboratory: Prof. Dr. Krzysztof Fitzner and Dr. Ewa Manko came from AGH University of Science and Technology, Krakow in Poland, and returned after a half year stay.

Presentations

Refining of Vanadium from V_2S_3 Using OS Process; T. Matsuura, T. Kikuchi, S. Natsui, and R. O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Hokkaido Univ., Sapporo, Hokkaido, Japan 17-18 Dec., 2015.

Calciothermic Reduction of TiS_2 in $CaCl_2$ Melt; N. Suzuki, H. Noguchi, M. Tanaka, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Fabrication of High-Density and High-Aspect-Ratio Anodic Alumina Nanofibers; D. Nakajima, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Nanocharacterization of Anodic Oxide Films Formed by Phosphonic Acid Anodizing; S. Akiya, T. Kikuchi, S. Natsui, N. Sakaguchi, R. O. Suzuki : ibid.

Three-dimensional SPH Simulation of Molten Metal-Slag Interfacial Flow Due to the Ascending Gas Bubble; R. Nashimoto, S. Natsui, T. Kikuchi, and R. O. Suzuki : ibid.

Fabrication of High-Aspect-Ratio Alumina Nanofibers; D. Nakajima, T. Kikuchi, S. Natsui, R. O. Suzuki : The 32nd Anodizing Research Society Conference, Himeji, Japan, Nov., 2014.

Grwoth Behavior of Anodic Oxide Films via Anodizing of Tungsten in Ethylene Glycol and Water Mixture Solution; J. Kawashima, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Effect of Gas Pressure in Furnace during Electrolysis for Reduction of Oxide; M. Kitamura, H. Noguchi, H. Hada, S. Natsui, T. Kikuchi, R. O. Suzuki and T. Uda : The 47th Symposium on Molten Salt Chemistry, Kobe University, Kobe, Hyogo, Japan, 28-29 Oct., 2015.

Calcium Rduction of TiS_2; N. Suzuki, H. Noguchi, M. Tanaka, S. Natsui, T. Kikuchi, R. O. Suzuki, and D. Matsuwaka : ibid.

CO Gas Enrichment by the Decomposition of CO_2 Gas with Molten Salt Electrolysis; F. Matsuura, S. Natsui, T. Kikuchi, and R. O. Suzuki : ibid.

Solid Electrolyte Anode Utilized for Reduction of $CaTiO_3$ by Electrolysis in $CaCl_2$-CaO Molten Salt; H. Hada, M. Kitamura, H. Noguchi, S. Natsui, T. Kikuchi, and R. O. Suzuki : ibid.

Particle-based Multiphase Flow Simulation for Low Carbon Ironmaking Design; S. Natsui, T. Kikuchi and R. O. Suzuki : Asia Steel International Conference 2015 (Asia Steel 2015), Yokohama, Japan, 5-8 Oct., 2015.

CO gas production by CO_2 gas decomposition in molten $CaCl_2$-CaO; F. Matsuura, S. Natsui, T. Kikuchi and R. O. Suzuki : 170th Annual Meeting of Iron and Steel Institute of Japan (Fall session), Ito Campus, Kyushu Univ., Hakata, Fukuoka, Japan, 16-18 Sept., 2015.

Using ZrO_2 solid electrolyte for reduction of $CaTiO_3$ by molten salt electrolysis; H. Hada, M. Kitamura, H. Noguchi, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Preparation of Low-Oxygen Ti via Sulfide by Molten Salt Electrolysis; R. O. Suzuki and D. Matsuwaka : ibid.

Particle Based Direct Numerical Modeling of Solid-Gas-Liquid 3-phases Flow; S. Natsui, R. Nashimoto, H. Takai, T. Kikuchi, R. O. Suzuki : ibid.

Influence of the Void Shape on Static Holdup; H. Takai, R. Nashimoto, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Microscopic Flow Analysis in Cohesive Zone of Blast Furnace; T. Kon, S. Natsui, S. Ueda, N. Maruoka and H. Nogami : ibid.

Analysis of Molten Metal - Slag Interfacial Flow due to the Gas Bubble Rising; R. Nashimoto, S. Natsui, H. Takai, R. O. Suzuki : ibid

Dendritic Nb Metal Formation by Calciothermic Reduction in $CaCl_2$ melt; N. Suzuki, S. Natsui, T. Kikuchi, and R. O. Suzuki : 157th Annual Meeting of Japan Institute of Metals (Fall session), Ito Campus, Kyushu Univ., Hakata, Fukuoka, Japan, 16-18 Sept., 2015.

Exploration for the Fabrication of Porous Alumina with High Regularity; S. Akiya, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Hydrodynamic Consideration of Liquid Metal－Molten Slag Interfacial Flow by the Movement of a Gas Bubble; S. Natsui, R. Nashimoto, T. Kikuchi and R. O. Suzuki : Shigen-Sozai 2015 (Annual Meeting of The Mining and Materials Processing Institute of Japan), Matsuyama, Japan, Sep. 2015.

Numerical analysis of matte - slag flow using smoothed particle hydrodynamics method; R. Nashimoto, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Fabrication of Highly Ordered Alumina Nanofibers via Two-Step Anodizing; D. Nakajima, T. Kikuchi, S. Natsui and R. O. Suzuki : The 132nd Annual Meeting of Surf. Finish. Soc. Jpn., Nagano, Japan, Sep., 2015.

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Structural Coloration of Aluminum and Nanoimprinting; T. Kikuchi, O. Nishinaga, S. Natsui and R. O. Suzuki : ibid.

Pipe-shaped Module Consisting of Trapezoidal Thermoelectric Elements; S. Oki and

R. O. Suzuki : 12th Annual Meeting of Thermoelectric Society of Japan, Tsukushi-Campus, Kyushu Univ., Kasuga, Fukuoka, Japan, 7-8 Sept., 2015.

Dynamic Analysis of Interfacial Tension Instability by Gas Bubble Passing through Molten Metal-Slag Interfaces; S. Natsui, R. Nashimoto, H. Takai, T. Kumagai, T. Kikuchi, and R. O. Suzuki : Conference of Metallurgists (COM 2015) Sustainability in Ironmaking/Steelmaking Symposium, 23-26, Aug. 2015, Fairmont Royal York Hotel, Toronto, Canada.

Optimization of Pipe-Typed Thermoelectric Generation Using Trapezoidal Elements; S. Oki, K. Ito, S. Natsui, and R. O. Suzuki : The Joint Summer Session of FY_2015 of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst., Muroran Inst. of Techn., Muroran, Hokkaido, Japan, 17 July, 2014.

Formation of Nb Dendrite Metal Using Calciothermic Reduction in $CaCl_2$ Melt; N. Suzuki, S. Natsui, T. Kikuchi, and R. O. Suzuki : ibid.

Fabrication of Aluminum with Rainbow Structural-Color Distribution; A. Takenaga, T. Kikuchi, S. Natsui and R. O. Suzuki : ibid.

Fabrication of High-Density and Highly Ordered Alumina Nanofiber Array; D. Nakajima, T. Kikuchi, S. Natsui and R. O. Suzuki : ibid.

Effect of Anodizing Condition on the Growth Behavior of Ordered Porous Alumina; S. Akiya, T. Kikuchi, S. Natsui and R. O. Suzuki : ibid.

Analysis of Interfacial Behavior Due to the Gas Bubble Passing through the Interface of Molten Metal-Slag; R. Nashimoto, S. Natsui, H. Takai, T. Kikuchi and R. O. Suzuki : ibid. (Poster, Encouraging prize)

Merit of Helical Configuration for Thermoelectric Generation; X.-N. Meng and R. O. Suzuki : 34th Annual International Conference on Thermoelectrics, (ICT2015) and 13th European Conference on Thermoelectrics (ECT2015), Dresden, Germany, June 28-2 July, 2015.

Numerical Optimization of Trapezoidal Thermoelectric Elements for Double-pipe Shape Module; S. Oki, K. O. Ito, S. Natsui, R. O. Suzuki : ibid.

Performance Analysis of the Thermoelectric Modules under Concentrated Radiation Heat Flux and Water Cooling; R. O. Suzuki, K. O. Ito, and S. Oki : ibid.

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Funahashi, Y. Matsumura, T. Barbier, S. Iwaoka, S. Katsuyama, R. O. Suzuki, and A. Kosuga : ibid.

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Oxide Reduction Using Electrolysis in $CaCl_2$-CaO or LiCl-Li_2O Melt; R. O. Suzuki (Plenary lecture) : 10th International Conference on Molten Salt Chemistry and Technology (MS10) and 5th Asian Conference on Molten Salts Chemistry and Technology (5AMS), Northeastern University, Shenyang, China, 10-14 June 2015.

CO_2 Decomposition by ZrO_2 Anode and Molten Salt Electrolysis in $CaCl_2$-CaO or LiCl-Li_2O; R. O. Suzuki, T. Uchiyama, T. Wakamatsu, F. Matsuura, M. Kitamura, K. Otake, S. Natsui, N. Sakaguchi, T. Kikuchi : ibid.

Instability of Molten Metal-Slag Interface Tension and Convection Influence; S. Natsui and R. Nashimoto : Invited lecture in Pan Pacific Copper Co., Ltd., Saganoseki, Oita, Japan, 22 May 2015.

Clarification of Dispersion Mechanisms of Melt in Packed Bed Using Particle Method Simulation; S. Natsui : 5th academic-industrial partnership symposium of Nippon Steel Sumitomo Metals, Futtsu, Chiba, March 23 2015.

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Influence of Interfacial Tension on the Molten Metal / Slag Interface Behavior Due to Rising Bubble; R. Nashimoto, H. Takai, T. Kikuchi and R. O. Suzuki : ibid.

CO Gas Production by the Decomposition of CO_2 Gas with Molten Salt Electrolysis; F. Matsuura, M. Kitamura, T. Wakamatsu, S. Natsui, T. Kikuchi, and R. O. Suzuki : 82th Autumn Meeting of Electrochem. Soc. of Jpn., Yokohama National University, Yokohama, Kanagawa, Japan, 15-17 March, 2015.

Regulation of Anode Gas at Reduction of Oxide by Electrolysis in $CaCl_2$-CaO

Molten Salt; H. Hada, H. Noguchi, S. Natsui, T. Kikuchi, and R. O. Suzuki : ibid.

Fabrication of Alumina Nanofibers by Anodizing; T. Kikuchi, D. Nakajima, J. Kawashima, O. Nishinaga, S. Natsui, N. Sakaguchi, R. O. Suzuki : The 131st Annual Meeting of Surf. Finish. Soc. Jpn., Yokohama, Japan, March, 2015.

Growth Mechanism of Alumina Nanofibers via Pyrophosphoric Acid Anodizing and Its Superhydrophilic Property; D. Nakajima, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Fabrication of Nanoporous Tungsten Oxide using Ammonium Nitrate; J. Kawashima, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Optimization of Thermoelectric Generation Module Considering Heat Radiation; S. Oki, K. Ito, and R. O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran Insti. Techn., Muroran, Hokkaido, Japan 29-30 Jan., 2015.

Calcium Reduction of Niobium Oxide Using Molten Calcium Chloride; N. Suzuki, S. Natsui, T. Kikuchi, and R. O. Suzuki : ibid.

Fabrication of Nanoporous Tungsten Oxide via Anodizing; J. Kawashima, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Growth Behavior of Alumina Nanofibers Fabricated by Anodizing in Pyrophosphoric Acid; D. Nakajima, T. Kikuchi, S. Natsui, R. O. Suzuki : ibid.

Anodizing in Etidronic Acid Solution and Structural Engineering; O. Nishinaga, T. Kikuchi, S. Natsui and R. O. Suzuki : The Winter Joint Meeting of the Hokkaido Branch of Academic Societies of Chemistry, Sapporo, Japan, Jan., 2015.

Facilities and Capabilities

X-ray diffractometer: Philips X’Pert Pro. A set for thin film XRD and powder XRD, and another set for high temperature XRD using Pt heating planer stage or Al_2O_3 crucible with RF heating.

Oxygen and Nitrogen Analyzer: LECO TC-600. Inert gas extraction with carbon crucible and infrared absorption method (5mass%-0.05 mass ppm).

Sulfur and Carbon Analyzer: LECO CS-600. Carbon and nitrogen are converted to CO and NO gas by burning in O_2 gas with RF heating and they are detected by the infrared absorption method.

CO/CO_2 Gas Analyzer IR-400: 4 sets. Yokogawa (0.1 vol%-100 %)
Gas Chromatography, Shimazu.

NO/SO_2 Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 1 vol%.

High voltage amplifier: Takasago Electrics. 100 V-8000 V.

Thermal Analyzers: SII EXSTAR-6000 TG/DTA. With Pt heater up to 1500 C.

Thermal Conductivity Measuring Unit: Kyoto Electrics. Hot disk method at room temperature.

Contact Angle Meter: Kyowa Interface Science, DM-501.

Atomic Force Microscope: SII NanoTechnology, Nanocute.

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Our group has been investigated various research subjects related to corrosion engineering, surface finishing of metals, and development of new technologies of electrochemistry related to energy and environment.

Current topics are followings:

(1) Effect of hydrogen absorption on semiconductor properties of the passive films formed in iron.

Hydrogen embrittlement of metals including high-strength steels used for automobiles and reactors has been an important issue. Effect of hydrogen absorption on the semiconductor properties of the passive films formed in iron was therefore investigated using photoelectrochemical technique. Pure iron foil was put in a Devanathan cell to charge hydrogen from backside. The passive film was formed on a front side by anodic polarization and impedance spectra and photocurrent spectra were measured as a function of hydrogen charging current and time. When hydrogen was charged, impedance and photocurrent were dropped temporary and then increased rapidly more than the rate without hydrogen charging. Photocurrent spectral data indicated that the decrease in photocurrent was occurred in an indirect transition range rather than the direct transition range. These results showed that hydrogen induced to the passive film from the substrate promotes temporal structural defects in the passive film to cause degradation of electronic barrier property and accelerates growth of the passive film.

(2) Corrosion monitoring of iron wire embedded in swelled bentonite clay

High level radioactive nuclear waste formed in nuclear power plants are planned to be stored in a carbon steel container, surrounded with thick cocoon of bentonite clay and installed deep underground around 500 m to separate their contents from human sphere for very long term as 10000 years. The containers will be exposed to bentonite swelled with underground water and high temperature induced by fission reaction of its contents up to 100 °C in an anaerobic environment. Such condition was reproduced in laboratory using a cell containing iron wire samples embedded in bentonite powder and heater. The cell was put in a globe box filled with nitrogen gas and pure water was supplied to the cell. Corrosion of iron wire was monitored using temperature compensated resistometry, corrosion potential, impedance spectra and coupling current between two iron wires in a few months. In the results, it was confirmed that the iron corroded almost constant rate even in a condition with very low oxygen content. Corrosion products contained not only oxide but also sulfide.

(3) Corrosion monitoring of reinforced steels in concrete structure

Maintenance, life control and elongation of infrastructures are important to establish sustainable modern society. Monitoring system to evaluate corrosion environment and corrosion rate of reinforcing steels embedded in concrete have been therefore developed. At first, gaseous condition inside the cement block was monitored using O_2, CO_2, temperature and relative humidity (RH) sensors. Iron foil was also put inside the block with splashed NaCl powder for corrosion monitoring by resistometry. The results showed that water penetrated from outside of the cement wall caused increase in RH level of inside atmosphere and initiated corrosion of iron foil. Oxygen level was dropped when iron corrosion progressed due to consumption of oxygen by the corrosion reaction and then increased gradually by gas penetration from outer atmosphere through the cement wall. On the other hand, CO_2 level decreased from ca. 2000 ppm at initial stage to stable level at ca. 1500 ppm due to absorption by cement. Impedance mapping inside cement block using eight iron wire electrodes embedded in a cement block was then performed. Two of eight wires were sequentially chosen and impedance spectra between them was measured with time. For example, penetration of water from the surface toward inside was traced from time-transition of impedance profile.

(4) Electrodeposition of Ti from ion electrode bath

Highly corrosion-resistive titanium is attractive as a coating metal. Since the reduction potential of Ti^{4+} ions to Ti is lower than the water decomposition potential, EMIC ionic liquid (I.L.) bath was used as plating bath. TiCl4 was mixed to EMIC and i-V curve was measured using Cu working electrode (WE), Ti counter electrode (CE) and Ag or Pt reference electrode (RE). Two cathodic peaks were observed assigned to two step reduction reaction of Ti^{4+} to Ti^{2+} and Ti^{2+} to Ti according to predecessors report. SEM observation of Cu-WE after cathodic polarization at proper potential showed deposits containing Ti and Ag when Ag-WE was used. Deposits containing Ti was also observed when Pt-RE was used although the amount of deposits was considerably less than that obtained with Ag-RE. These results seemed to indicate that Ti was co-deposited with Ag which might be dissolved from Ag-RE in the I.L. bath under electrolysis condition. Pulse polarization increased considerably an amount of deposits containing Ti and Ag when Ag-RE was used but not the case of Pt-RE.

(5) Electrochemical CO_2 reduction in hydrophobic ionic liquid

EMIm-TFSI I.L. was known to absorb CO_2 gas and thus considered as an electrolyte medium for electrochemical CO_2 reduction. Two compartments electrochemical cell composed of I.L. bath bubbled with CO_2 gas including Cu cathode and and KOH aqueous solution bath including Pt anode separated with a proton conducting Nafion membrane was used for efficient reduction. Gas phase in the I.L. cell was sampled and fed to a gas chromatograph for compositional analysis. The results confirmed that the most of the product was CH_4 and reduction rate depended on not only polarization potential but also distance of Cu cathode from the membrane surface in I.L. bath. This indicated that the transportation of H^+ from membrane surface to Cu cathode was a one of the major factor for conversion efficiency in the water-poor I.L. solvent. When Ni cathode was used instead of Cu, major product was H_2 but not CH_4.

(6) Development of Al-air battery suppressing self-discharging

Metal-air batteries using light metals such as Li, Mg and Al have been paid attention because of their very high theoretical energetic density. Among them Al has advantages in its rich natural resource and trivalent ionic state which provides large energetic density. Al-air battery using aqueous solution electrolyte could be, however, self-discharged even in the non-operation condition by the dissolution reaction in concentrated alkaline electrolyte solution. In this study, therefore, an I.L. electrolyte was applied for Al-air battery to avoid this undesirable dissolution reaction. Two compartments test cell composed of a compartment including Al-negative electrode, I.L., and KOH pellets and another compartment including KOH solution and positive air electrode separated with an anion-exchange membrane was built. Hydrophobic EMIm-TFSI and hydrophilic EMISE were examined as I.L. bath. In I.L. compartment, dissolution reaction of Al could be proceeded only when a small amount of water was added and ceased when water was consumed up. Test cell connected to an electronic load cell showed operation current in the order of 10 mA.

Presentation

Extension of Electrochemical Techniques to Atmospheric Corrosion; K. Azumi: 18th Seoul National University-Hokkaido University Joint Symposium, Seoul National Univ., Nov. 26-27, 2015.

Photoelectrochemical Analysis of Atmosphere-Corroded Metals; T. Kato, and K. Azumi: ibid.

Composition control of alloy coatings electrodeposited from EMIC ionic liquid bath; Y. Sato, K. Azumi: 129th annual meeting of the Japan Institute of Light Metals, Tsudanuma, Nov. 21-22, 2015.

Electrochemical CO_2 Reduction in EMIN-TFSI Ionic Liquid; K. Azumi, H. Yoshikawa, K. Suetake: The 66th Annual Meeting of ISE, Taipei, Taiwan, Oct. 4-9. 2015.

Al-Zn coating using a double counter electrode electrodeposition system from ionic liquid bath; Y. Sato, K. Azumi: NTTHX Joint Symposium, Urumqi, Xinjiang, China, Aug. 8-11, 2015.

Electrochemical reduction of CO_2 absorbed in an ionic liquid; H. Yoshikawa, K. Azumi: *ibid*.

Characterization of electrochemical CO_2 reduction in Emim-TFSI ionic liquid bath; H. Yoshikawa, K. Azumi: Winter Joint Meeting of the Hokkaido Branch of the Chemistry Related Societies, Sapporo, Jan.27-28, 2015.

Development of Al-air battery using ionic liquid; S. Oguma, K. Azumi: *ibid*.

Application of Coupling photocurrent method to atmospheric corrosion; K. Azumi, S. Yamazoe: Aurora Seminar, Trondheim., Norway, Jan. 18-21, 2015.

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In April, Mr. Masaaki Goto and Mr. Hajime Nishimura entered Graduate School of Chemical Sciences and Engineering, Hokkaido University and Ms. Tomomi Kanazawa joined the laboratory. In March, Dr. Jun-Seob Lee obtained the degree of Ph.D from Hokkaido University.

The research activities of the laboratory are directed to an understanding of the mechanism and kinetics of the heterogeneous interfacial reactions, and to the development of the microelectrochemical techniques for well-understanding the reactions. The research activity is also directed to an understanding of the mechanism and kinetics in wet corrosion of practical materials including steels and titanium alloys.

Current topics on research are as follows:

(1) Heterogeneous Formation and Dissolution of Oxide Film on Polycrystalline Iron

High temperature treatment of polycrystalline iron in air forms a relatively thick oxide film. Heterogeneous electrochemical properties of the film and heterogeneous dissolution behavior of the film in acid were investigated by microelectrochemistry with a micro-capillary cell and electrochemical two-dimensional ellipsometry.

(2) *In-situ* Observation of Passive Titanium Surface by an Ellipso-microscope and Photo-electrochemical Modification of the Surface by Scanning UV-light Irradiation

Photo-corrosion of an anodized titanium surface in 0.01 mol dm^{-3} sulfuric acid solution was investigated with an *in-situ* electrochemical ellipso-microscope. Local irradiation of UV-light on an anodized surface under potentiostatic polarization allowed the flow of a photo-induced anodic current and changed the brightness and made a spot in the image. This indicates that the irradiation promotes photo-electrochemical oxidation, resulting in a change in the thickness and/or structure of the oxide film on the surface. Two-dimensional ellipsometry revealed that the film change was dependent not only on power density of the irradiation light but also on electric charge consumed for the reaction.

(3) Development of Liquid Phase Ion-gun for Local Sulfidation of Metal Surface

Microelectrode technique for local sulfidation of metallic materials was developed. Cathodic polarization of a silver-silver sulfide microelectrode successfully generated hydrogen sulfide ions in neutral solution. In the vicinity of the specimen surface, the amount of ions generated could be controlled by electric charge, while the concentration of ions was dependent on geometrical conditions of both microelectrode and specimen surface. The technique was applied to local sulfidation of silver surface and type 316 L stainless steel.

(4) Fabrication of Multichannel Microelectrode-array and Its Application

Scanning probe technique such as a scanning electrochemical microscope (SECM) enables to visualize the electrochemical activity on a specimen electrode. However, it is not suitable to pursuit the relatively rapid reaction of the electrode such as an initiation of pitting corrosion. In order to overcome this problem, a microelectrode-array has been fabricated by MEMS technologies in collaboration with Nanotechnology Platform, Waseda University. Simultaneously, a numerical calculation of diffusion problem on the microelectrode array has been conducted. A 16x16-channels array structure with a microelectrode diameter of 10 µm successfully showed limiting currents flowing through 256 microelectrodes independently. Interference effect between electrodes in the array was also simulated. These results have been used to re-design the array.

(5) Exploring New SECM Redox Mediator for Passive Surface

SECM is an effective tool for investigating the passive surface. Conventionally, it has been used to image the surface by combination of redox mediator of ferro- or ferri-cyanide ions. In order to extend the application of SECM in corrosion research, new method and new mediator are explored. One of candidates for new redox mediator is ferrocenemethanol. DFT of ferrocenemethanol as well as other mediator molecules was carried out and revealed the dependence of the redox potential on HOMO state of the molecule. Cyclic voltammetry revealed that kinematic constant of ferrocenemethanol was larger than that of ferro-/ferri-cyanide ions, though these mediators had similar redox potentials. It was also confirmed in SECM image, because ferrocenemethanol showed a better lateral resolution during SECM imaging of passive surface on dual phase carbon steel.

(6) Convection-dependent Hydrogen Permeation into a Carbon Steel Sheet

In order to avoid hydrogen embrittlement of carbon steel sheet, basic research for mechanism and kinetics of hydrogen penetration in the steel is necessary. The Devanathan-Stachurski double electrochemical cell for measurement of hydrogen-permeation into the sheet was extended to an electrolyte-flowing design. Hydrogen-permeation was actualized by a sinusoidal perturbation of the flow rate of the entry cell. The hydrogen-permeation response, i.e., phase shift of the detection current from the entry current, was analyzed numerically and applied to local measurement with a micro-capillary cell technique. Numerical calculation for simulation of the local measurement revealed that hydrogen diffusion coefficient at a grain boundary was five-order in magnitude larger than that at a single grain.

(7) Quantitative Effect of Anions in Corrosion of Iron

The roles of anions such as sulfate and chlorides in mass-transport process of iron corrosion were investigated using microelectrode technique. The shape of dynamic polarization curve of electrode in weak acid was strongly dependent on the size of the electrode as well as applied potential. Quasi-passivation was observed at lower potential with a smaller electrode, indicating that promoted active dissolution results in concentration of corrosion products and suppression of the further dissolution. Tafel slope of dynamic polarization curves was also analyzed to investigate the role of anions in charge transfer process of iron dissolution.

Other Activities

Dr. K. Fushimi attended to Aurora Seminar, Tronhein-Tromso, Norway in January, and to Eurocorr 2015, Graz, Austria and to CAMP-ISIJ, Fukuoka, Japan in September. In October, Dr. K. Fushimi, Mr. J.-S. Lee and Mr. Y. Yamamoto attended to 66th ISE Meeting, Taipei, Taiwan and Dr. K. Fushimi, Mr. J.-S. Lee and Mr. Y. Takabatake attended to 288th ECS Meeting, Phoenix, AZ. Mr. Y. Yamamoto attended 18th Hokkaido Univ.-Seoul National Univ. Joint Symposium, Seoul, Korea in November.

Presentations

Anisotropic corrosion of anodizing iron and titanium surface; K. Fushimi: International seminar on surface science, passivity and corrosion of metals “Aurora Seminar”, MS Kong Harald, Trondheim-Tromso, Norway, Jan. 18-20, 2015.

Local porous type anodic oxide films formation with solution flow type micro-droplet cell; M. Sakairi, T. Yamaguchi, F. Nishino, R. Itzinger, K. Fushimi: ASST 2015 VII Aluminium Surface Science & Technology, Madeira, Portugal, May 17-21, 2015.

Hydrodynamic Effect of Entry Side Cell on Hydrogen Permeation into Steel Sheet; K. Fushimi, M. Jin, Y. Yamamoto, Y. Kitagawa, T. Nakanishi, Y. Hasegawa: Eurocorr 2015, Graz, Austria, Sep. 6-15, 2015.

Hydrodynamic Perturbation for Local Detection of Hydrogen Permeation into Steel Sheet; K. Fushimi, M. Jin, Y. Yamamoto: CAMP-ISIJ Recent progress of hydrogen-passive surface on steels to prevent hydrogen embrittlement, Fukuoka, Japan, Sep. 18-20, 2015.

Photo-electrochemical Degradation of Anodized Titanium Surface Observed using EIS and Ellipso-microscopy; K. Fushimi, H. Ikeyama, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, M. Ueda, T. Ohtsuka: 66th Annual Meeting of the International Society of Electrochemistry, Taipei, Taiwan, Oct. 4-9, 2015.

Passivation Behavior of Type-316L Stainless Steel in Presence of Hydrogen Sulfide Ions Generated from Liquid-Phase Ion Gun; J.-S. Lee, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Fushimi: 66th Annual Meeting of the International Society of Electrochemistry, Taipei, Taiwan, Oct. 4-9, 2015.

Local Measurement of Hydrogen Diffusion in Steel Sheet; Y. Yamamoto, M. Jin, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Fushimi: 66th Annual Meeting of the International Society of Electrochemistry, Taipei, Taiwan, Oct. 4-9, 2015.

Effect of Hydrogen Sulfide Ions on a Passivation Behavior of Type-316L Stainless Steel; J. -S. Lee, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Fushimi: 228th ECS Meeting, Phoenix, AZ, Oct. 11-15, 2015.

Heterogeneous Thermal Oxide Film Formed on Polycrystalline Pure Iron; Y. Takabatake, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Fushimi: 228th ECS Meeting, Phoenix, AZ, Oct. 11-15, 2015.

Effect of Fluctuation of Electrolyte Flow Rate in Hydrogen Entry Cell on Hydrogen Permeation into Steel Sheet; K. Fushimi, Y. Yamamoto, M. Jin, Y. Kitagawa, T.

Nakanishi, Y. Hasegawa: 228th ECS Meeting, Phoenix, AZ, Oct. 11-15, 2015.

Local Hydrogen Penetration Measurement on Steel Sheet Using Sine Wave Perturbation Method; Y. Yamamoto, M. Jin, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Fushimi : The 18th Hokkaido University - Seoul National University Joint Symposium, Seoul, Korea, Nov. 27, 2015.

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Mr. Hareesh Parepalli, School of Mechanical Sciences, Indian Institute of Technology Bhubaneswar, India, joined our group as internship student form 11th May 2015 to 16th July 2015.

Research work of our group directs toward (1) effect of metal cations on passive film structure of metals in model fresh water, (2) effect of CH_3COONa concentration on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments, (3) effect of surface condition on hydrogen permeation behavior of zinc coated steels during cyclic wet and dry corrosion (4) formation of layer structured porous type anodic alumina locally by solution flow type micro-droplet cell, (5) effect of water layer thickness and temperature on oxygen reduction reaction on zinc, 6) formation of multi-layer structure of Cu-Ni with nano-size thickness and its property, and 7) field exposer test in cold and heavy snow district.

Current topics on research are in the following:

(1) Effect of metal cations on passive film structure of metals in model tap water

The effects of metal cations on corrosion of metals in model fresh water were investigated by electrochemical techniques and immersion tests. Surface analysis was carried out by X-ray photoelectron spectroscopy (XPS). Analysis of XPS showed metal cations that have large hardness of cations are incorporated in passive films. The electrochemical and immersion results showed that the used hardness of cations is not suitable as a corrosion indicator of metals. Therefore, a new corrosion indicator, “corrosion inhibitory effect of cations, Y”, that consists of X and molar volume ratio, ΔV, have been proposed. The proposed indicator is explain well the corrosion rate of metals in fresh water.

(2) Effect of solution chemistry on oxide film composition of 13 % Cr stainless steel in model oil and gas environments

The investigation of the effect of immersion period and on the surface structure by electrochemical and surface analysis techniques. There was the plateau region of the current density in the anodic polarization curves, and the current density decreased with increasing CH_3COONa concentration. No difference in value of the plateau region of the current density by addition of CO_2 was observed in solutions with CH_3COONa. Pitting potential shifted to the positive direction as increasing CH_3COONa concentration, and showed the lower value by adding CO_2.The Cr enriched layer formed on the samples surface after immersion test, and the thickness of the layer became thinner as increasing CH_3COONa concentration. From FT-IR observation, the CH_3COO^- and HCO_3^- adsorbed on the most outer surface was confirmed.

(3) Hydrogen permeation behavior metals investigated by Lase irradiation and micro-electrochemical cell.

A constant dew point type wet and dry corrosion test was applied to investigate the effects of scratches and specimen composition on the hydrogen permeation behavior of coated steels as well as of uncoated steel. A laser machining technique was used to form a size controlled scratch on specimens. Independent of the specimen composition and the area of the formed scratches, the hydrogen permeation current was observed, and the corrosion products were also observed after the tests. The hydrogen permeation current of the steels with the formed scratches decreased with number of cycles of the wet and dry tests. It was suggested that the composition, scratch, and corrosion products play an important role in the hydrogen permeation behavior during wet and dry corrosion.

An area-selective technique for electrochemical hydrogen detection with focused pulse YAG laser irradiation has been newly developed. The developed technique was applied to measure hydrogen permeation behavior of iron at selected areas. The hydrogen permeation current was detected after the laser irradiation, suggesting that indirect activations of hydrogen generation and entry reactions were produced by the focused pulse YAG laser irradiation. An obtained hydrogen diffusion coefficient was in good agreement with previously reported of iron. The results suggested that diffusion coefficient was depend on grain structure.

(4) Formation of layer structured porous type anodic alumina locally by solution flow type micro-droplet cell

A solution flow-type micro droplet cell with co-axial dual capillary tubes (Sf-MDC) was applied to form porous type anodic alumina film with layered structure at selected areas on aluminum. The anodizing process with different repetition numbers, yielding different oxide layer numbers was performed with the Sf MDC. The investigation of cross sections of the formed oxide showed that the pore diameter widened at the boundary between layers. From a simulated anodizing process with the Sf-MDC, the reason for this modification of the pores was suggested to be intermittent anodizing with processes of drying up of the solution of the pores and widening at the bottom of the pores. The fine structure of the pore strongly depends on the composition of used solution.

(5) Effect of water layer thickness and temperature on oxygen reduction reaction on zinc

The micro electrode technique was applied to investigate oxygen limiting current changes with both water layer thickness and substrate temperature. The water layer thickness was controlled from 1 mm to 0.2 mm. The oxygen limiting current with thin water layer significantly increased at low temperature such as 273 K. The tendency of the limiting current change with temperature and water layer thickness do not change with concentration.

(6) Multi-layer structured of Cu-Ni with nano-size thickness film formation and its property

A thickness controlled Cu-Ni or Fe-Cr multi-layer was formed on Ti substrate by DC electro-deposition, and also investigate diffusion behavior of formed films and mechanical property. Film structure and morphology were observed by RBS and SEM. The diffusion rate of formed films are faster than that expected by literature data. The tensile strength of the films are almost same as that expected from Cu-Ni alloy, and crack initiation and propagation were observed by laser microscope.

(7) Field exposer test in cold and heavy snow district

The filed exposer test for corrosion of steels in cold and heavy snow district as Sapporo and Akkeshi in Hokkaido is carrying out in this year. This exposer test is a joint research work with NIMS. A one year exposure tests sample was finished and new exposure samples of each steels have been started. As a results, corrosion rate in heavily snow and cold area depends on concentration of sea born salt and not linearly depends on temperature.

Other activities

In January, Assoc. Prof. Sakairi attended International seminar on surface science, passivity and corrosion of metals (Aurora), Norway and presented a paper entitled "Formation of layer structured porous type anodic alumina by Sf-MDC".

In May, Assoc. Prof. Sakairi attended Aluminum surface science and technology 2015, ASST2015, Madeira, Portugal and presented tow papers entitled "Formation of oxide films for high capacitance aluminum electrolytic capacitor by liquid phase deposition and anodizing" and "Local porous type anodic oxide films formation with solution flow type micro-droplet cell".

In September, Assoc. Prof. Sakairi organized international organized session of "Recent progress of hydrogen-passive surface on steels to prevent hydrogen embrittlement" in ISIJ autumn meeting, Hakata, Japan, and presented a paper entaitled "Hydrogen permeation behavior of steels with formed scratch during wet and dry corrosion".

In September, Assoc. Prof. Sakairi attended EUROCORR2015 at Graz, Austria, and presented a paper entitled "Surface analysis of passive films formed on Aluminum alloys in different metal cation contained solutions".

In October, Assoc. Prof. Sakairi attended Asian steel 2015 at Yokohama Japan, and presented a paper entitled "Resent research progress in creation of hydrogen-passive surfaces on steels to prevent of hydrogen embrittlement".

In October, Assoc. Prof. Sakairi gave a lecture entitled "Analysis of corrosion behavior of coated steels -focused on Hydrogen embrittlement-" at The 223th and 224th Nishiyama mimorial technical lecture, ISIJ, Tokyo and Osaka.

In November, Assoc. Prof. Sakairi attended 4th Hokkaido University - Seoul National University Joint Symposium, Seoul, Korea, and presented a paper entitled "Area selective anodizing of aluminum by solution slow type micro-droplet cell".

Presentations

Formation of layer structured porous type anodic alumina by Sf-MDC, M. Sakairi, T. Yamaguchi, F. Nishino and R. Itzinger, International seminar on surface science, passivity and corrosion of metals(Aurora), Norway, January, 2015.

Electrochemical behavior of 13Cr stainless steel in acid NaCl solution, H. Mizukami, M. Sakairi, and S. Hashizume, The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, January, 2015.

Fine structure of locally formed porous alumina formed by Sf-MDC, F. Nishino, M. Sakairi, R. Itzinger, The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, January, 2015.

Effect of inner wall composition on anodizing behavior of Ti-Al micro-channel, I, Yamamori, T. Ohomi, M. Sakairi, K. Iwai, he Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, January, 2015.

Effect of solution flow on anodizing behavior of Ti-Al micro-channel, H. Matsuoka, T. Ohomi, M. Sakairi, K. Iwai, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, January, 2015.

Hydrogen permeation behavior of steels during wet-dry cyclic corrosion tests, K. Igarashi and M. Sakairi, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, January, 2015.

Effect of solution flow on anodic oxide film structure formed on Ti-Al micro-channel wall, H. Matsuoka, T. Ohomi, M. Sakairi, and K. Iwai, The 169th spring meeting of ISIJ, Tokyo, March, 2015.

Corrosion research of Steels using micro-electrochemistry, M. Sakairi, Nishiyama memorial prize lecture, The 169th spring meeting of ISIJ, Tokyo, March, 2015.

Interface reaction and electrochemical detection of hydrogen generation and permeation into steels during wet/dry corrosion, 2015 Spring meeting of The Japan Institute of Metals, Tokyo, March 2015 (Invited).

Effect of metal cations in model fresh water on passive film structure formed on Al alloy, M. Sakairi, R. Sasaki, and A. Kaneko, The 82th meeting of The Electrochemical Society of Japan, Yokohama, March, 2015.

Effect of solution chemistry on electrochemical behavior of Al alloy in model tap water, K. Otani, R. Sasaki, M. Sakairi, A. Kaneko, The Hokkaido Sec. of Light metal soc., Chitose, April, 2015.

Hydrogen permeation behavior at scratch formed on coated steels during wet/dry corrosion, K. Igarashi and M. Sakairi, Zairyo-to-kankyo 2015 meeting, Tokyo, May, 2015.

Effect of CO_2 on corrosion behavior of 13Cr stainless steel in acid NaCl solutions, H. Mizukami, M. Sakairi, and S. Hashizume, Zairyo-to-kankyo 2015 meeting, Tokyo, May, 2015.

Formation of oxide films for high capacitance aluminum electrolytic capacitor by liquid phase deposition and anodizing, M. Sakairi, R. Fujita, T. Kikuchi and S. Nagata, ASST2015, Madeira, Portugal, May, 2015.

Local porous type anodic oxide films formation with solution flow type micro-droplet cell, M. Sakairi, T. Yamaguhchi, F. Nishino, L. Itzinger, K. Fushimi, ASST2015, Madeira, Portugal, May, 2015.

Analysis of surface oxide films formed on Al alloy in different cations containing model fresh water, K. Otani, M. Sakairi, R. Sasaki, and A. Kaneko, Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem., Hakodate, July, 2015.

Effect of CO_2 on electrochemical behavior of 13Cr stainless steel in acid NaCl, H. Mizukami, M. Sakairi, and S. Hahiszume, The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, July, 2015.

Effect of thin solution layer on corrosion behavior of Zn coated steels, R. Sakaki, M. Sakairi, J. Tsujino, The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, July, 2015.

Hydrogen permeation behavior of scratch formed Zn-Al coated steel during wet/dry corrosion, K. Igarashi and M. Sakairi, The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, July, 2015.

Surface analysis of passive films formed on Aluminum alloys in different metal cation contained solutions, M. Sakairi, R. Sasaki and K. Suzuki, and A. Kaneko, Eurocorr2015, Graz, Austria, September, 2015.

M. Sakairi and K. Igarashi, Hydrogen permeation behavior of steels with formed scratch during wet and dry corrosion, International session, ISIJ autumn meeting, Fukuoka, September, 2015.

Effect of metal cations on EIS behavior of surface films formed on Al in model tap water, K. Otani and M. Sakairi, The 83th meeting of The Electrochemical Society of

Japan, Fukaya, September, 2015.

Research of corrosion and surface treatment by micro-electrochemical methods, M. Sakairi, The 83th meeting of The Electrochemical Society of Japan, Fukaya, September, 2015 (Invited)

Resent research progress in creation of hydrogen-passive surfaces on steels to prevent of hydrogen embrittlement, M. Sakairi, Asian steel 2015, Yokohama, Japan, October, 2015 (Invited).

Structure changes of passive film formed on Al alloy by metal cations, M. Sakairi, R. Sasaki, K. Otani, and A. Kaneko, The 129th Autumn meeting of Jpn. Light Metal Soc., Tsudanuma, November, 2015.

Structure changes of corrosion products formed on Al alloy by metal cations, K. Otani, M. Sakairi, and A. Kaneko, The 129th Autumn meeting of Jpn. Light Metal Soc., Tsudanuma, November, 2015.

Analysis of surface film formed on 13 Cr stainless steel in acid NaCl solutions with CO_2, H. Mizukami, M. Sakairi, and S. Hashizume, The 62th discussion meeting of Zairyo-to-Kankyo, Fukuoka, November, 2015.

Corrosion morphology of metals change by Zn^{2+} in model tap water, K. Otani, M. Sakairi, and A. Kaneko, The 62th discussion meeting of Zairyo-to-Kankyo, Fukuoka, November, 2015.

Effect of thickness of thin solution layer on oxygen reduction reaction on Zn electrode, R. Sakaki, M. Sakairi, J. Tsujino, The 62th discussion meeting of Zairyo-to-Kankyo, Fukuoka, November, 2015.

Investigation of hydrogen permeation behavior of steels with laser irradiation, K. Igarashi, M. Sakairi, and H. Nagao, The 62th discussion meeting of Zairyo-to-Kankyo, Fukuoka, November, 2015.

Structure of anodic oxide film formed on Ti-Al micro-channel wall with anodizing time, I. Yamamori, T. Ohmi, M. Sakairi, and K. Iwai, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, December, 2015.

Effect of Zn^{2+} on corrosion morphology of carbon steel during immersion test, K. Otani and M. Sakakairi, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, December, 2015 (Had student presentation prize).

ABSTRACT of PUBLICATIONS

Electroplating of Al-Zr alloys in $AlCl_3$-NaCl-KCl molten salts to improve corrosion resistance of Al

M. Ueda, T. Teshima, H. Matsushima and T. Ohtsuka

Journal of Solid State Electrochemistry, **19**, 3485-3489 (2015)

To improve the corrosion resistance of Al in chloride solutions, electrodeposition of Al-Zr alloys of various compositions was carried out at 448 K by constant potential control in $AlCl_3$-NaCl-KCl molten salt containing $ZrCl_4$. Cathodic reduction of the Zr ions starts at a potential of 0.4 V vs. Al/Al(III) in the molten salt. The electrodeposition of Al and Zr occurred at potentials more negative than -0.02 V. The concentration of Zr in the electrodeposit increased to 23 at% at -0.02 V. In the XRD analysis, the electrodeposits formed at -0.05 to -0.15 V had good crystallinity, the electrodeposits containing higher concentrations of Zr formed at -0.02 or -0.04 V show an amorphous or fine crystal structure. The pitting potentials of Al-Zr alloys containing 5-23 at% Zr in 0.1 M NaCl solution shifted from +0.1 to +0.3 V compared with those of pure Al.

In Situ Observation of Dynamic Meniscus Front Interface in Alkaline Fuel Cell

H. Matsushima, W. Majima, Y. Fukunaka and M. Ueda

ECS Electrochemistry Letters, **4**, F43-F45 (2015)

Controlling the wetting properties at the three-phase interface is important for improving the performance of alkaline fuel cells. The meniscus of a potassium hydroxide droplet was formed on a nickel electrode, and the interference fringe during the oxygen reduction reaction was observed by confocal laser microscopy. The high spatial resolution of the microscope revealed thin film formation at the meniscus front interface. The thickness decreased with increasing cathodic potential. The generation of microscopic convection by interfacial surface tension may affect mass transfer in the thin film.

Carbon Nanotube Synthesis via the Calciothermic Reduction of Carbon Dioxide with Iron Additives

Tatsuya Kikuchi, Ryoma Ishida, Shungo Natsui, Takehiko Kumagai, Isao Ogino,
Norihito Sakaguchi, Mikito Ueda, and Ryosuke Suzuki

ECS Solid State Letters, **4**, M19-M22 (2015)

The novel fabrication of multi-walled carbon nanotube (MWCNT)/cementite (Fe_3C) nanocomposites was demonstrated via the calciothermic reduction of carbon dioxide (CO_2) through electrolysis in molten $CaCl_2$/CaO with iron additives at 1173 K. In this technique, CO_2 generated from a graphite anode is reduced to carbon with a metallic calcium reductant formed on a graphite cathode via electrolysis in molten salt. Calciothermic reduction without iron additives resulted in the formation of onion-like carbons (OLCs) with spherical graphite layers and thin graphite sheets. In contrast, MWCNT/Fe_3C nanocomposites and OLCs were successfully fabricated via calciothermic reduction with iron additives through their catalytic activities.

[DOI: 10.1149/2.0031509ssl]

Protection of an AZ91D substrate by an intermediate Zn layer for Al plating from an $AlCl_3$–NaCl–KCl molten salt bath

Yu Hang, Hiroki Murakoshi, Mikito Ueda, Kazuhisa Azumi

Surface and Coatings Technology, **270**, 164-169 (2015)

An intermediate protective layer of Zn was formed on the AZ91D surface to prevent dissolution of the substrate surface and to obtain a uniform deposition layer of Al in an electroplating process from a molten salt bath. Simple zincate treatment did not result in the formation of a Zn layer with sufficient thickness and coverage for substrate protection. Electrodeposition of Zn was thus conducted after the zincating process to thicken the Zn layer. A Zn layer of a few μm in thickness sufficiently protected the AZ91D substrate. A uniform Al layer was then electrodeposited on Zn-protected AZ91D without degradation of the substrate. Since the Mg alloy surface and Zn surface were not sufficiently active for Zn deposition and Al deposition, respectively, Cu-nanoparticle predeposition was applied to each surface before the electrodeposition processes.

Electrorefining of sodium in sodium bis(trifluoremethanesulfonyl)imide and tetrabutylammonium bis(trifluoremethanesulfonyl)imide mixture ionic liquids for metallic sodium recycling

M. Ueda, R. Inaba, H. Matsushima and T. Ohtsuka

ECS Electrochemistry Letters, **4**, E1-E3 (2015)

To develop an electrorefining process for sodium to enable recycling of used sodium-sulfur batteries, a non-aqueous electrolyte with low melting point was investigated. A mixed ionic liquid of NaTFSI (sodium bis (trifluoromethane) sulfonylimide) - TBATFSI(tetrabutylammonium bis (trifluoromethane) sulfonylimide) was selected for the electrolyte. From AC impedance measurements, a maximum ionic conductivity of 16 mS cm^{-1} was established of 20 mol% NaTFSI -TBATFSI concentration at 433 K. Electrorefining for 20 hours was carried out with a stable voltage under constant current electrolysis. Liquid pure sodium was electrodeposited by the constant current electrolysis. The calcium content in the sodium cathode was decreased from 250 to 52 ppm by the electrorefining.

Titanium surface anodized under UV light irradiation observed by ellipso-microscopy

K. Fushimi, K. Kurauchi, H. Ikeyama, Y. Kitagawa, T. Nakanishi, Y. Hasegawa,
M. Ueda, and T. Ohtsuka,

J Solid State Electrochem, **19**, 3579–3587 (2015)

Photo-corrosion of an anodized titanium surface in 0.05 mol dm^{-3} sulfuric acid solution was investigated by using an in situ electrochemical ellipso-microscope. Irradiation of ultra-violet (UV) light on an anodized surface, which showed a patch-like bright image on an ellipso-microscopic view due to non-uniform growth of the oxide film, under potentiostatic polarization allowed the flow of a photo-induced anodic current and changed the brightness and patch pattern in the image. This indicates that the irradiation promotes photo-electrochemical reaction, resulting in a change in the thickness and/or structure of the oxide film on the surface. The film change was dependent not only on power density of the irradiation light but also on applied potential during the irradiation and crystallographic orientation of the substrate. Pitting initiation during potentiodynamic polarization in the acid with bromide ions was also monitored using the ellipso-microscope. The irradiation resulted in pitting initiation at lower potentials than those in a non-irradiated condition.

Preparation of low-platinum-content platinum-nickel, Platinum-cobalt binary alloy and platinum-nickel-cobalt ternary alloy catalysts for oxygen reduction reaction in polymer electrolyte fuel cells

Mu Li, Yanhua Lei, Nan Sheng, Toshiaki Ohtsuka

Journal of Power Sources, **294**, 420-429 (2015)

A series of low-platinum-content platinum-nickel (Pt-Ni), platinum-cobalt (Pt-Co) binary alloys and platinum-nickel-cobalt (Pt-Ni-Co) ternary alloys electrocatalysts were successfully prepared by a three-step process based on electrodeposition technique and studied as electrocatalysts for oxygen reduction reaction (ORR) in polymer-electrolyte fuel cells. Kinetics of ORR was studied in 0.5 M H_2SO_4 solution on the Pt-Ni, Pt-Co and Pt-Ni-Co alloys catalysts using rotating disk electrode technique. Both the series of Pt-Ni, Pt-Co binary alloys and the Pt-Ni-Co ternary alloys catalysts exhibited an obvious enhancement of ORR activity in comparison with pure Pt. The significant promotion of ORR activities of Pt-Ni and Pt-Co binary alloys was attributed to the enhancement of the first electron-transfer step, whereas, Pt-Ni-Co ternary alloys presented a more complicated mechanism during the electrocatalysis process but a much more efficient ORR activities than the binary alloys.

The Effect of Impurity Concentration and Cr Content on the Passive Oxide Films in Ferritic Stainless Steels

Toshiaki Ohtsuka, Masatoshi Abe, and Tomohiro Ishii

Journal of The Electrochemical Society, **162**(10), C528-C535 (2015)

The properties of passive oxides on three steels consisting of 11%Cr, 18%Cr, and 30%Cr-2%Mo were studied in acidic sulfate solution by the Mott-Schottky relation for semiconducting properties, potential modulation reflectance (PMR) spectroscopy for light absorption properties, X-ray photoelectron spectroscopy (XPS) for composition estimation, and Fe^{3+}/ Fe^{2+} redox current measurement for properties of electron transfer. The influence of the impurity concentration in the steels was also studied. The donor density in n-type semiconducting passive oxides as estimated from the Mott-Schottky plot decreased with a higher Cr content and with a lower impurity concentration. Cr enrichment occurred in the passive oxide and, for example, for 30Cr-2Mo steels, the ratio of Cr ions to total metallic ions in the passive oxide was approximately 70 wt%. The light absorption edge of the passive oxide measured by PMR was approximately 2.4 eV, irrespective of the Cr content and impurity concentration. The redox current on the passive oxide was much inhibited compared with that on the Pt electrode. The redox current decreased in a similar manner as the donor density. The inhibition of the redox current was assumed to be due to the space charge layer in the n-type semiconducting passive oxide.

Monitoring the development of rust layers on weathering steel using in situ Raman spectroscopy under wet-and-dry cyclic conditions

Toshiaki Ohtsuka and Shozo Tanaka

J Solid State Electrochem, **19**, 3559-3566 (2015)

The change of rust composition on weathering steel was consecutively monitored by in situ Raman spectroscopy during exposure to atmosphere under cyclic 4 h wet-4 h dry condition for 144 h in the presence of NaCl deposit. Raman spectra of the rust surface in the presence of NaCl deposit at 0.93 mg cm^{-2} corresponded to those of lepidocrocite (γ -FeOOH) and magnetite (Fe_3O_4) in the initial 12 h exposure. After 12 h exposure, akaganeite (β -FeOOH) started to form, and its molar ratio on the rust surface increased to 90% at 30 h exposure. The Raman spectra further changed after 30 h exposure in which γ -FeOOH again emerged. The reappearance of γ -FeOOH is assumed to be caused by capture of chloride ions in β -FeOOH resulting in the decrease of free chloride ions in the surface solution layer. When the amount of NaCl deposit was decreased to 0.11 mg cm^{-2}, the surface was covered with dark brown corrosion product which may be amorphous FeOOH and after repeated dry-wet cycles, yellowbrown spots emerged which consisted of β -FeOOH.

In-situ Measurement of Corrosion Products on Metals by Raman Spectroscopy

Toshiaki Ohtsuka

Journal of the Surface Science Society of Japan, **36**, 12-17 (2015)

The corrosion of metallic materials is caused by action of aqueous or gaseous environment and the products of the corrosion greatly depend on the environmental condition. It is desired that the identification of the products is done under the in-situ environmental condition. Raman Spectroscopy is one the methods to identify them under the condition. The application of Raman spectroscopy to detection of the corrosion products of steel, zinc, and titanium is introduced. (Japanese)

The Influence of Composition on Band Gap and Dielectric Constant of Anodic Al-Ta Mixed Oxides

A. Zaffora, F. Di Franco, M. Santamaria, H. Habazaki and F. Di Quarto

Electrochimica Acta, **180**, 666-678 (2015)

Al-Ta mixed oxides were grown by anodizing sputter-deposited Al-Ta alloys of different composition. Photocurrent spectra revealed a band gap, E_g, slightly independent on Ta content and very close to that of anodic Ta_2O_5 (~4.3 eV) with the exception of the anodic film on Al-10at% Ta, which resulted to be not photoactive under strong anodic polarization. The photoelectrochemical characterization allowed to estimate also the oxides flat band potential and to get the necessary information to sketch the energetic of the metal/oxide/electrolyte interfaces. Impedance measurements allowed to confirm the formation of insulating material and to estimate the dielectric constant of the oxides, which resulted to be monotonically increasing with increasing Ta content (from 9 for pure Al_2O_3 to 30 for pure Ta_2O_5).

Highly Durable Platelet Carbon Nanofiber-Supported Platinum Catalysts for The Oxygen Reduction Reaction

E. Tsuji, T. Yamasaki, Y. Aoki, S.-G. Park, K. Shimizu and H. Habazaki

Carbon, **87**, 1-9 (2015)

We report the preparation and characterization of highly durable platinum catalysts supported on platelet-structure carbon nanofibers (Pt/p-CNFs) for the oxygen reduction reaction. The p-CNFs were prepared by liquid phase carbonization of polyvinyl chloride using a porous anodic alumina template at 600°C; their degree of graphitization was increased by the subsequent heat treatment at higher temperatures of up to 1400°C. The platinum nanoparticles with ~3 nm diameter were deposited more uniformly on the p-CNFs compared with those on the commercial Ketjen black (KB). The catalytic activity and durability of the Pt/p-CNFs for the oxygen reduction reaction (ORR) in H_2SO_4 solution were improved by increasing the heat-treatment temperature of p-CNFs. The durability of the Pt/p-CNFs was much higher than that of Pt/KB; in particular, a loss of less than 10% was observed in the ORR activity of Pt/p-CNF heat-treated at 1400°C after potential cycling from 0.5 to 1.5 V vs. RHE for 200 cycles in an argon-saturated H_2SO_4 aqueous solution.

CO_2 Methanation of Ni Catalysts Supported On Tetragonal ZrO_2 Doped with Ca^{2+} and Ni^{2+} Ions

H. Takano, H. Shinomiya, K. Izumiya, N. Kumagai, H. Habazaki and
K. Hashimoto

International Journal of Hydrogen Energy, **40**, 8347-8355 (2015)

This paper reports highly active CO_2 methanation catalysts of Ni supported on tetragonal ZrO_2 for supply of renewable energy in the form of CH_4 via electrolytic H_2 generation. The Ni/tetragonal ZrO_2 catalysts with the nominal cationic compositions of 50 at.% Ni-(Zr + Ca) (Ca/(Zr + Ca) molar ratios of 0.125-0.333), were prepared by calcination of a ZrO_2 sol mixed with nickel and calcium nitrates at 650 and 800 degrees C and subsequent H_2 reduction of NiO. All the catalysts prepared exhibited almost 100% CH_4 selectivity, and the activity increased with the calcium content up to a Ca/(Zr + Ca) molar ratio between 0.167 and 0.200, above which the activity tended to decrease. At the optimized calcium content, a tetragonal ZrO_2 phase with cation vacancies introduced by Ca^{2+} and Ni2+ doping was predominant, in addition to fcc Ni. A monoclinic ZrO_2 phase was also present below the optimized calcium content, while a Ca-rich amorphous or $CaZrO_3$ phase was formed with tetragonal ZrO_2 above the optimized calcium content. The high catalytic activity of the catalyst with the optimized composition could be correlated with the presence of tetragonal ZrO_2 with oxygen vacancies.

Formation and Field-Assisted Dissolution of Anodic Films on Iron in Fluoride-Containing Organic Electrolyte

K. Shahzad, E. Tsuji, Y. Aoki, S. Nagata and H. Habazaki

Electrochimica Acta, **151**, 363-369 (2015)

Magnetron-sputtered iron films were potentiodynamically anodized at two different sweep rates to 50 V in an ethylene glycol electrolyte containing ammonium fluoride and water. At a high sweep rate of 1.0 V s^{-1}, a barrier-type anodic film was formed even though the current efficiency was as low as similar to 50%. In contrast, a nanoporous anodic film developed at a low sweep rate of 0.05 V s^{-1}, and the film-formation efficiency reduced to 37%. The main part of the anodic films consists of iron (III) hydroxyfluoride with a thin inner layer composed of FeF_3. The inner fluoride layer is formed owing to the faster inward migration of fluoride ions compared to that of the oxygen species. During immersion or re-anodizing of the iron specimen with an approximately 100-nm-thick, barrier-type anodic film at and below 15 V, thinning of the anodic film proceeded uniformly and film dissolution was enhanced by applying an electric field. The impact of the electric field on film formation and dissolution is discussed.

Control of the Physical Properties of Anodic Coatings Obtained by Plasma Electrolytic Oxidation on Ti_6Al_4V Alloy

D. Quintero, O. Galvis, J. A. Calderón, M. A. Gómez, J. G. Castaño, F. Echeverría and H. Habazaki

Surface and Coatings Technology, **283**, 210-222 (2015)

Spark anodizing on Ti_6Al_4V has been performed in three alkaline solutions using different electrical parameters in order to study the coating formation. The surface features show a dependence on the shape and distribution of the electric microdischarges. In addition, the surface features and the chemical composition of the coatings are dependent on the anodizing solution employed. The tribological properties of the coatings formed are correlated with the morphology and the internal structure of the coatings. The variation of the internal structure of the coatings was evidenced by EIS analysis. Results indicate that it is possible to control the physical properties of the anodic film by an adequate selection of the process parameters. A porous structure is obtained using a solution mainly composed of hypophosphite, which exhibits a good tribological performance. Low porosity and compact structure can be obtained in the anodic film by using an anodizing solution composed of hypophosphite and metasilicate; furthermore, these coatings exhibit a good corrosion protection. Highly porous structure is achieved by using an anodizing solution composed of hypophosphite and sulfate. The best wear resistances were observed in coatings formed at potentiostatic mode, as demonstrated by the results of ball-on-disc wear tests.

Behavior of Alloying Elements during Anodizing of Mg-Cu and Mg-W Alloys in a Fluoride/Glycerol Electrolyte

M. S. Palagonia, A. Němcová, I. Kuběna, M. Šmíd, S. Gao, H. Liu, X. L. Zhong,
S. J. Haigh, M. Santamaria, F. D. Quarto, H. Habazaki, P. Skeldon and
G. E. Thompson

Journal of The Electrochemical Society, **162**, C487-C494 (2015)

Anodizing of sputtering-deposited magnesium and Mg-0.75at.% Cu and Mg-1.23at.% W alloys has been carried out in a fluoride/glycerol electrolyte. The aims of the study were to investigate the enrichment of alloying elements in the alloy immediately beneath the anodic film and the migration of alloying element species in the film. The specimens were examined by electron microscopy and ion beam analysis. An enrichment of copper is revealed in the Mg-Cu alloy that increases with the anodizing time up to ~6×10^{15} Cu atoms cm^{-2}. Copper species are then incorporated into the anodic film and migrate outwards. In contrast, no enrichment of tungsten occurs in the Mg-W alloy, and tungsten species are immobile in the film.

Synthesis and Characterization of Carbon Black/Manganese Oxide Air Cathodes for Zinc–Air Batteries: Effects of The Crystalline Structure of Manganese Oxides

P.-C. Li, C.-C. Hu, H. Noda and H. Habazaki

Journal of Power Sources, **298**, 102-113 (2015)

Manganese oxides (MnO_x) in α-, β-, γ-, δ-MnO_2 phases, Mn_3O_4, Mn_2O_3, and MnOOH are synthesized for systematically comparing their electrocatalytic activity of the oxygen reduction reaction (ORR) in the Zn–air battery application. The optimal MnO_x/XC-72 mass ratio for the ORR is equal to 1 and the oxide crystalline structure effect on the \ORR is compared. The order of composites with respect to decreasing the ORR activity is: α-MnO_2/XC-72 > γ-MnO_2/XC-72 > β-MnO_2/XC-72 > δ-MnO_2/XC-72 > Mn_2O_3/XC-72 > Mn_3O_4/XC-72 > MnOOH/XC-72. The textural properties of MnO_x are investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 adsorption/desorption isotherms with Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Electrochemical studies include linear sweep voltammetry (LSV), rotating ring-disk electrode (RRDE) voltammetry, and the full-cell discharge test. The discharge peak power density of Zn–air batteries varies from 61.5 mW cm^{-2} (α-MnO_2/XC-72) to 47.1 mW cm^{-2} (Mn_3O_4/XC-72). The maximum peak power density is 102 mW cm^{-2} for the Zn–air battery with an air cathode containing α-MnO_2/XC-72 under an oxygen atmosphere when the carbon paper is 10AA. The specific capacity of all full-cell tests is higher than 750 mAh g^{-1} at all discharge current densities.

Corrosion Protection of Iron Using Porous Anodic Oxide/Conducting Polymer Composite Coatings

Y. Konno, E. Tsuji, Y. Aoki, T. Ohtsuka and H. Habazaki

Faraday Discussions, **180**, 479-493 (2015)

Conducting polymers (CPs), including polypyrrole, have attracted attention for their potential in the protection of metals against corrosion; however, CP coatings have the limitation of poor adhesion to metal substrates. In this study, a composite coating, comprising a self-organized porous anodic oxide layer and a polypyrrole layer, has been developed on iron. Because of electropolymerization in the pores of the anodic oxide layer, the composite coating showed improved adhesion to the substrate along with prolonged corrosion protection in a NaCl aqueous corrosive environment. The anodic oxide layers are formed in a fluoride-containing organic electrolyte and contain a large amount of fluoride species. The removal of these fluoride species from the oxide layer and the metal/oxide interface region is crucial for improving the corrosion protection.

GDOES Depth Profile Analysis of Interfacial Enrichment of Copper during Anodizing of Al-Cu Alloy

H. Habazaki, M. Uemura, K. Fushimi, E. Tsuji, Y. Aoki and S. Nagata

Journal of Surface Finishing Society of Japan, **66**, 670-672 (2015)

The present study demonstrates the quantitative evaluation of the amount of copper atoms accumulated in a thin alloy layer, ~1.5 nm thick, immediately beneath the anodic films up to 120 nm thickness by GDOES depth profile analysis. This has been conducted so far only by RBS, which is not readily available, and GDOES provides another method to examine the interfacial process in anodizing of binary aluminum alloys.

Formation of Self-Organized Porous Anodic Films on Iron and Stainless Steel

H. Habazaki, K. Shahzad, T. Hiraga, E. Tsuji and Y. Aoki

ECS Transactions, **69**, 211-223 (2015)

High purity iron and commercial Type 304 and 430 stainless steels were anodized in ethylene glycol electrolytes containing fluoride and water. When iron was anodized in the electrolytes containing relatively high water concentrations (≥1.5 mol dm^{-3}) at 50 V, porous anodic films with scalloped metal/film interface were developed. In contrast, the anodic films formed in the electrolytes with low water concentrations (≤0.5 mol dm^{-3}) resulted in the flat metal/film interface. In addition, the interpore distance became smaller with respect to the thickness of barrier layer when the water concentration is reduced. These morphological changes may be associated with the change in the composition of the anodic films. Anodizing of stainless steels was dependent upon the type of stainless steel; a steady-state current continued up to ~160 V on Type 430 stainless steel, while exponential current increase occurred above ~50 V on Type 304 stainless steel during potentiodynamic anodizing. The thickness of the barrier layer and the morphology of the porous layer were largely dependent upon the type of stainless steel. Based on such findings, the mechanism of film growth was discussed.

Growth of Barrier-Type Anodic Films on Magnesium in Ethylene Glycol Electrolytes Containing Fluoride and Water

H. Habazaki, F. Kataoka, K. Shahzad, E. Tsuji, Y. Aoki, S. Nagata, P. Skeldon
and G. E. Thompson

Electrochimica Acta, **179**, 402-410 (2015)

This study demonstrates the formation of uniform barrier-type anodic films on magnetron-sputtered magnesium films at high current efficiency in ethylene glycol electrolytes containing 0.1 mol dm^{-3} NH_4F and various concentrations (0.1–28 mol dm^{-3}) of H_2O. The anodic films containing a crystalline MgF_2 phase develop both at the metal/film and film/electrolyte interfaces due to simultaneous migrations of anions inwards and cations outwards, respectively. When Mg −1.2 at% Au/Mg bilayer film is anodized, initial prior oxidation of magnesium proceeds with gold atoms accumulating in a thin layer beneath the anodic film. The accumulated gold atoms are incorporated into the anodic film as a band when the alloy layer is completely anodized. Fluoride-containing gold species are formed by the incorporation and the gold species migrate outwards at a rate of 0.4 times the rate of Mg^{2+} ions. The addition of phosphate in the electrolyte results in the formation of an amorphous anodic film, and the phosphate incorporated into the anodic film is distributed throughout the film thickness. The transport number of cations is also influenced by the phosphate incorporation.

Particle-based Multiphase Flow Simulation for Low Carbon Ironmaking Design

S. Natsui, T. Kikuchi and R. O. Suzuki

Proceedings of Asia Steel International Conference 2015, 298-299 (2015)

Ironmaking technology is currently focused on the introduction of the decreased reducing agent operation of a blast furnace in order to decrease CO_2 emissions. Because the coke ratio is reduced in this operation, causing a huge pressure drop, it has become increasingly important to understand the in-furnace phenomena using the non-empirical method. In this study, the DEM-CFD simulation was carried out to analyse the heat and mass transfer between the gaseous phase and the particles in a packed bed. In particular, the effect of recently proposed helical structure of coke and ore layers was compared with the traditional layer-by-layer structure. It was found that the increase of the gas flow rate in a large grain size coke layer, would not affect the total permeability of the packed bed. Since the helical structure decreases the amount of inflow of the gaseous phase to the ore bed, the reduction rate of this ore tends to decrease the thickness of the layered structure, but this effect is relatively small. The helical structure becomes more permeable, if a thicker layer is maintained even under the decreased coke ratio condition.

Blast Furnace Modeling by Euler-Lagrange Method

S. Natsui, T. Kikuchi and R. O. Suzuki

Bulletin of the Japan Institute of Metals, **54**(9), 432-435 (2015)

Discrete element-type model such as discrete element method (DEM) and particle method are expected to enable precisely simulation of the discontinuous and inhomogeneous phenomena in the recent operating conditions. With discrete models, microscopic information on each particle in the packed bed can be obtained in addition to the overall phenomena in the blast furnace. Visual information for understanding in-furnace phenomena can be also obtained with high spatial resolution. Liquid dripping and the movement of fines in the lower part of the blast furnace can be simulated with high accuracy by using DEM and particle methods such as the moving particle semi-implicit Method (MPS). Moreover, the optimum bed structure for low reducing agent operation is being clarified by application of the Eulerian-Lagrangian method.

Prefatory Note – To Realize the Thermoelectric Power Generation

R. O. Suzuki

Journal of Japan thermoelectric society, **12**(1), 1 (2015).

Several requisites and limitations are described to overcome the discussing issues to realize the thermoelectric power generation. The materials properties should be brushed up to obtain the better performance, however, the design for thermoelectric generation device is also critical as well as the national resources of materials. The steady steps to improve the design of modules and devices are required to open new burst in this field.

Model Study of the Effect of Particles Structure on the Heat and Mass Transfer through the Packed Bed in Ironmaking Blast Furnace

S. Natsui, H. Takai, R. Nashimoto, T. Kikuchi, and R. O. Suzuki

International Journal of Heat and Mass Transfer, **91**, 1176-1186 (2015).

Ironmaking technology is currently focused on the introduction of the decreased reducing agent operation of a blast furnace in order to decrease CO_2 emissions. Because the coke ratio is reduced in this operation, causing a huge pressure drop, it has become increasingly important to understand the in-furnace phenomena using the non-empirical method. In this study, the DEM-CFD simulation was carried out to analyse the heat and mass transfer between the gaseous phase and the particles in a packed bed. In particular, the effect of recently proposed helical structure of coke and ore layers was compared with the traditional layer-by-layer structure. This comparison shows that the helical structure is effective for the smooth gas flow in the packed bed. It was found that the increase of the gas flow rate in a large grain size coke layer, would not affect the total permeability of the packed bed. Since the helical structure decreases the amount of inflow of the gaseous phase to the ore bed, the reduction rate of this ore tends to decrease the thickness of the layered structure, but this effect is relatively small. The helical structure becomes more permeable, if a thicker layer is maintained even under the decreased coke ratio condition.

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Fabrication of a novel aluminum surface covered by numerous high-aspect-ratio anodic alumina nanofibers

D. Nakajima, T. Kikuchi, S. Natsui, N. Sakaguchi and R. O. Suzuki

Applied Surface Science, **356**, 54-62 (2015)

The formation behavior of anodic alumina nanofibers via anodizing in a concentrated pyrophosphoric acid under various conditions was investigated using electrochemical measurements and SEM/TEM observations. Pyrophosphoric acid anodizing at 293 K resulted in the formation of numerous anodic alumina nanofibers on an aluminum substrate through a thin barrier oxide and honeycomb oxide with narrow walls. However, long-term anodizing led to the chemical dissolution of the alumina nanofibers. The density of the anodic alumina nanofibers decreased as the applied voltage increased in the 10 to 75 V range. However, active electrochemical dissolution of the aluminum substrate occurred at a higher voltage of 90 V. Low temperature anodizing at 273 K resulted in the formation of long alumina nanofibers measuring several micrometers in length, even though a long processing time was required due to the low current density during the low temperature anodizing. In contrast, high temperature anodizing easily resulted in the formation and chemical dissolution of alumina nanofibers. The structural nanofeatures of the anodic alumina nanofibers were controlled by choosing of the appropriate electrochemical conditions, and numerous high-aspect-ratio alumina nanofibers (>100) can be successfully fabricated. The anodic alumina nanofibers consisted of a pure amorphous aluminum oxide without anions from the employed electrolyte.

Optimum Exploration for the Self-Ordering of Anodic Porous Alumina Formed via Selenic Acid Anodizing

S. Akiya, T. Kikuchi, S. Natsui and R. O. Suzuki

Journal of The Electrochemical Society, **162**, E244-E250 (2015)

Improvements of the regularity of the arrangement of anodic porous alumina formed by selenic acid anodizing were investigated under various operating conditions. The oxide burning voltage increased with the stirring rate of the selenic acid solution, and the high applied voltage without oxide burning was achieved by vigorously stirring the solution. The regularity of the porous alumina was improved as the anodizing time and surface flatness increased. Conversely, the purity of the 99.5-99.9999 wt% aluminum specimens without second phases of metals and metallic compounds was not affected by the regularity of the porous alumina formed by selenic acid anodizing. The porous alumina was also self-ordered on/around a defect, such as a grain boundary, under self-ordering high voltage anodizing conditions. A highly ordered cell arrangement measuring 111 nm in diameter was successfully fabricated over the whole aluminum surface by selenic acid anodizing using a 99.999 wt% aluminum plate at 273 K and 46 V for 24 h under vigorous stirring conditions.

CO_2 Decomposition by ZrO_2 Anode and Molten Salt Electrolysis in $CaCl_2$-CaO or LiCl-Li_2O

R. O. Suzuki, T. Uchiyama, T. Wakamatsu, F. Matsuura, M. Kitamura,
K. Otake, S. Natsui, N. Sakaguchi, and T. Kikuchi

Proc. 10th Intern. Conf. on Molten Salt Chemistry and Technology (MS10) and 5th Asian Conf. on Molten Salt Chem. and Tech.(AMS5), 10-14 June, 2015, Northeastern University, Shenyang, China, 218-223 (2015).

The electrochemical decomposition of carbon dioxide gas in either $CaCl_2$-CaO or LiCl-Li_2O molten salt with the assistance of oxygen ionic conductor such as Y_2O_3-stabilized ZrO_2 is examined as a fundamental study. This process consists of two parallel mechanisms of CO_2 decomposition. First mechanism is the combination of thermal reduction of CO_2 gas by metallic Ca and the electrochemical reaction to recover Ca from CaO. Another mechanism is a dissolution of CO_2 gas as CO_3^{2-} ions and the successive electrochemical decomposition of CO_3^{2-} at the cathode. The first mechanism is dominant at the dilute CaO concentration, but at the higher CaO content, CaO binds CO_2 gas in the melt as CO_3^{2-} ions which are subsequently electrolyzed. The current efficiency of this process approached 98%. The product, i.e., solid carbon, is deposited on the cathodic surface as the carbon nano-tubes, thin plate or spherical amorphous carbon. The latter was recovered also at the melt surface. Carbon deposition decreased the electronic conductivity between two electrodes, and the reaction rate decreased significantly.

Oxide reduction using electrolysis in $CaCl_2$-CaO or LiCl-Li_2O melt

R. O. Suzuki,

Proc. 10th Intern. Conf. on Molten Salt Chemistry and Technology (MS10) and 5th Asian Conf. on Molten Salt Chem. and Tech.(AMS5) 10-14 June, 2015, Northeastern University, Shenyang, China, 1-4 (2015). (Plenary Lecture).

Electrochemical decomposition of oxides at the cathode was examined, especially when using $CaCl_2$-CaO molten salt system. By applying the voltage larger than the decomposition potential of CaO, CaO dissolving in $CaCl_2$ melt can be decomposed to metallic Ca and O^{2-}. When carbon is chosen as the anode, O^{2-} reacts with C to form CO or CO_2 gas at the anode surface. The decomposition voltage of CaO for CO/CO_2 gas formation is as low as 1.4 V. The deposited Ca at the cathode is found as the “metal fog” near the cathode, when Ca dissolution is delayed. Usually this deposit dissolves into the $CaCl_2$ melt due to the wide solubility range, and forms a strong reducing environment at the vicinity of the cathode. Calciothermic reduction by this dissolved Ca is essential for reduction of the oxide placed at the cathode. Ca-rich $CaCl_2$ melt is effective for oxide reduction. The by-product CaO often forms the complex oxides, such as $CaTiO_3$ and Ca_2TiO_4, with the residual oxides.

Performance Analysis of Thermoelectric Modules Using Polyhedron Elements

X.-N. Meng, R. O. Suzuki

Materials Transactions, **56** (7), 1092-1095 (2015).

This study proposed new thermoelectric (TE) module configurations consisting of polyhedron elements, and examined the TE performance of them by conducting the finite-element analysis. The performance of TE module in the case of symmetrically arranging the polyhedron elements is slightly higher than that of arranging elements in parallel. The heat transfer and electric resistance, respectively, depend on the module configuration and element shape, and affect the TE performance simultaneously. TE performance increases significantly when the internal resistance becomes smaller and the heat diffuses slower. dx.doi.org/10.2320/matertrans.E-M2015808

Self-ordered Aluminum Anodizing in Phosphonoacetic Acid and Its Structural Coloration

A. Takenaga, T. Kikuchi, S. Natsui and Ryosuke O. Suzuki

ECS Solid State Letters, **4**, P55-P58 (2015)

Ordered anodic porous alumina with large-scale periodicity was fabricated via phosphonoacetic acid anodizing. Aluminum specimens were anodized in a 0.1-0.9 M phosphonoacetic acid solution under various electrochemical operating conditions, and optimum anodizing at 205-225 V exhibited self-ordering growth of the porous alumina. These self-ordering voltages during phosphonoacetic acid anodizing filled an undiscovered vacant region in the linear relationship between the self-ordering voltage and the cell diameter. The nanostructured aluminum surface formed via self-ordering phosphonoacetic acid anodizing produced a bright structural coloration with a visible light wavelength of 500-700 nm, which is useful for optical nanoapplications.

Durability of Silicide-based Thermoelectric Modules at High Temperatures in Air

R. Funahashi, Y. Matsumura, T. Barbier, T. Takeuchi, R. O. Suzuki,
S. Katsuyama, A. Yamamoto, H. Takazawa and E. Combe

J. Electronic Materials, **44**(8), 2946-2952 (2015).

Thermoelectric modules consisting of n-type $Mn_{2.7}Cr_{0.3}Si_4Al_2$ and p-type $MnSi_{1.75}$ legs have been fabricated by use of composite pastes of Ag with Pt or Pd. For the module prepared by Ni-B plating and with Ag paste, the specific power density reached 370 mW/cm^2 at a heat-source temperature of 873 K. Ni-B plating 5 μm thick on the surfaces of the silicide legs reduced both the internal resistance and degradation of the power generated by silicide modules at temperatures up to 873 K in air. This is because of oxidation of Al diffusing into the n-type legs and reaching the Ag electrodes on both the hot and cold sides. Ni-B plating can suppress Al diffusion into n-type legs. However, cracking was observed parallel to the contact surface in the middle of the Ni-B plating layer on the p-type legs. It was also found that incorporating Pt or Pd into the Ag paste effectively suppressed degradation of the contact resistance between the silicide legs and the Ag electrodes.

dx.doi.org/10.1007/s11664-015-3784-7

Development of Thermoelectric Technology from Materials to Generators

R. Funahashi, C. Wan, F. Dang, H. Anno, R. O. Suzuki, T. Fujisaka
and K. Koumoto,

Advanced Materials for Clean Energy, Chapter 4,
Edited by Qiang Xu and Tetsuhiko Kobayashi, CRC Press, 83-142 (2015)

This work reported a calculation method and results for the optimization of cascade structures and compared 1D analytical and 2D numerical calculations. The TE material dimensions and number of p-n pairs are optimized using 1D analysis, and the optimal condition depends on the combination and performance of the TE materials. When TE materials with a higher performance are used in the cascade module, the optimization procedure becomes crucial and is effective in enhancing the conversion efficiency. We emphasize the importance of module design as well as development of TE materials. It is expected that this work will encourage to open up new application areas which recover unused heat, in particular, over a wide temperature range such as 1200–300 K.

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Polymer nanoimprinting using an anodized aluminum mold for structural coloration

T. Kikuchi, O. Nishinaga, S. Natsui and R. O. Suzuki

Applied Surface Science, **341**, 19-27 (2015)

Polymer nanoimprinting of submicrometer-scale dimple arrays with structural coloration was demonstrated. Highly ordered aluminum dimple arrays measuring 530 to 670 nm in diameter were formed on an aluminum substrate via etidronic acid anodizing at 210 to 270 V and subsequent anodic oxide dissolution. The nanostructured aluminum surface led to bright structural coloration with a rainbow spectrum, and the reflected wavelength strongly depends on the angle of the specimen and the period of the dimple array. The reflection peak shifts gradually with the dimple diameter toward longer wavelength, reaching 800 nm in wavelength at 670 nm in diameter. The shape of the aluminum dimple arrays were successfully transferred to a mercapto-ester ultra-violet curable polymer via self-assembled monolayer coating and polymer replications using a nanoimprinting technique. The nanostructured polymer surfaces with positively and negatively shaped dimple arrays also exhibited structural coloration based on the periodic nanostructure, and reflected light mostly in the visible region, 400-800 nm. This nanostructuring with structural coloration can be easily realized by simple techniques such as anodizing, SAM coating, and nanoimprinting.

Highly Ordered Anodic Alumina Nanofibers Fabricated via Two Distinct Anodizing Processes

D. Nakajima, T. Kikuchi, S. Natsui and R. O. Suzuki

ECS Electrochemistry Letters, **4**, H14-H17 (2015)

Fabrication of high-density, highly ordered anodic alumina nanofibers was demonstrated via two distinct anodizing processes: porous and fibrous oxide formations. Highly ordered aluminum dimple arrays were fabricated via sulfuric/oxalic acid anodizing and selective porous alumina dissolution. Subsequent pyrophosphoric acid anodizing using the nanostructured aluminum surface caused anodic alumina nanofibers to grow preferentially at the six apexes of the ordered hexagonal aluminum dimples under the appropriate electrochemical conditions. Well-defined, high-density, highly ordered anodic alumina nanofibers with 37-75 nm periodic spacing and at densities of 1.4-5.6 × 10^{14} m^{-2} were successfully fabricated on the aluminum surface via two distinct anodizing processes.

CO Gas Production by Molten Salt Electrolysis from CO_2 Gas

F. Matsuura, T. Wakamatsu, S. Natsui, T. Kikuchi and R. O. Suzuki

ISIJ International, **55**(2), 404-408 (2015)

CO_2 gas is decomposed to CO and C by the molten salt electrolysis using $CaCl_2$-CaO and solid state electrolyte, zirconia, as the anode. Partially CO_2 gas dissolves to form CO_3^{2-} and it is electrochemically decomposed to carbon. The other portion of CO_2 gas bubbles reacts with metallic Ca electrochemically deposited near the cathode, and forms C or CO gas. By increasing the flow rate of CO_2 gas to the reactor, a high concentration of CO gas is generated. By increasing the concentration of CO_2 gas in the initial gas, a large amount of CO gas was produced in the exhaust gas, and its rate approached to 3.32×10^{-8} m^3/s in our experimental setup. These experimental evidences reflect the electrochemical decomposition of CO_3^{2-} in the molten salt.
dx.doi.org/10.2355/isijinternational.55.404

Reduction Behavior of Packed Bed of Sinter Reduced by CO-CO_2-H_2-H_2O-N_2 gas

T. Kon, R. Saito, S. Ueda, S. Natsui, R. Inoue and T. Ariyama

ISIJ International, **55**(6), 1213-1222 (2015).

To mitigate CO_2 emission from a blast furnace, the use of H_2 as a reducing agent is considered to be a prominent method. Reduction of iron ore was reported to be improved by H_2 addition. In the present research, reduction in a sinter-packed bed by CO and H_2 was carried out under various oxygen partial pressures, and the influence of reduction atmosphere on the reaction behavior was investigated. It was confirmed that the reduction rates were higher when using H_2/H_2O and $CO/CO_2/H_2/H_2O$ mixtures than when using a CO/CO_2 gas mixture. The reaction rate constant for iron ore reduction was determined from the experimental result using a numerical model. The influence of the water-gas shift reaction on the reduction rate was analyzed by comparing the results obtained using the numerical model and those in the experiments. Moreover, the longitudinal distribution of the reaction rate in the packed bed was analyzed to examine the influence of the water-gas shift reaction.

dx.doi.org/10.2355/isijinternational.55.1213

Influence of Shape of Cohesive Zone on Gas Phase State in the Blast Furnace Analyzed by DEM-CFD Model

S. Ueda, T. Kon, H. Kurosawa, S. Natsui, T. Ariyama, and H. Nogami

ISIJ International, **55**(6), 1232-1236 (2015).

Maintaining gas permeability is an important issue to realize low coke rate operation of blast furnace. In present study, the melting behavior of the iron ore and the layer structure in low coke rate operation were introduced in to the DEM-CFD model, and then behaviors of gas and moving bed in the blast furnace were simulated. Influence of shape of cohesive zone in low coke rate operation was investigated, and the effect of coke slit in the cohesive zone on gas flow was demonstrated in the calculation result. Surface area of cohesive zone and intersection angle between the burden layers and cohesive zone will determine the activity of coke slit.
dx.doi.org/10.2355/isijinternational.55.1232

Characterization of Liquid Trickle Flow in Poor-wetting Packed Bed

S. Natsui, T. Kikuchi, R. O. Suzuki, T. Kon, S. Ueda and H. Nogami

ISIJ International, **55**(6), 1259-1266 (2015).

A low coke rate operation of a blast furnace tends to cause deterioration of the gas permeability. The liquid iron and molten slag dripping under the melting zone influences the gas flow and permeability in the lower part of the furnace. A computational fluid dynamic model, using a particle-based simulation, is presented for characterization of the melt dripping behavior in a packed bed. In this work, the validity of the liquid passing conditions based on the gravity to surface tension ratio was confirmed. The melt shape produces an “icicle,” “droplet,” and “dome” forms based on the change of the surface tension and density absolute values. Even with an identical liquid volume passage, the form of the liquid flow changed by the pressure from the liquid’s upper portion. Even if it has identical gravity and surface tension ratios, the liquid flow changes with the volume of the liquid phase and its form.
dx.doi.org/10.2355/isijinternational.55.1259

Droplet Motion on Non-smooth Solid Surface

S. Ueda, T. Kon, S. Kikuchi, S. Natsui, S. Sukenaga and H. Nogami

ISIJ International, **55**(6), 1277-1283 (2015).

Liquid dripping in a packed bed of coke in a blast furnace decreases the gas permeability and production stability. Enhancing the liquid flow is desirable to increase the productivity of the blast furnace process. The wettability between the liquid and coke affects the dripping behavior. In present study, the contact angle of a moving droplet on a non-smooth solid surface was investigated considering dripping slag and pig iron droplets in a packed bed of coke. The advancing and receding contact angles of water and mercury on a substrate were measured at room temperature while controlling the wettability and roughness. The angles between the cut surface of the coke and water or mercury were also measured. The roughness of the solid surface affected the movement of the adhering droplets, but the effect of the roughness was significantly altered by the wettability. It was found that the resistance to movement of the liquid increased and decreased under good and poor wettability conditions, respectively. Because the wettability of the liquid phase in the blast furnace changed depending on the temperature and composition of molten slag or iron, the force on a liquid droplet from the coke surface changed depending on the position and composition of the hot metal and molten slag in the coke bed.

dx.doi.org/10.2355/isijinternational.55.1277

Analysis of Effect of Packed Bed Structure on Liquid Flow in Packed Bed Using Moving Particle Semi-implicit Method

T. Kon, S. Natsui, S. Ueda and H. Nogami

ISIJ International, **55**(6), 1284-1290 (2015).

Liquid flow in blast furnaces has a significant influence on gas flow and pressure drop. Therefore, the stability of blast furnace operations and productivity are affected by liquid flow. In a furnace, liquid flows in a packed bed consisting of coke. Holdup is an important phenomenon in packed bed flow. It changes with the variation of the packed bed structure and the physical properties of the liquid. In this study, a numerical simulation for packed bed flow is carried out. The effects of a packed bed structure on holdup phenomena were analyzed by the moving particle semi-implicit (MPS) method.

dx.doi.org/10.2355/isijinternational.55.1284

Analysis of Powder Motion in a Packed Bed of Blast Furnace Using the Discrete Element Method

S. Kikuchi, T. Kon, S. Ueda, S. Natsui, R. Inoue and T. Ariyama

ISIJ International, **55**(6), 1313-1320 (2015).

Owing to powder accumulation in the packed bed, the permeability of gas and liquid deteriorates, which decrease throughput of the blast furnace. Powder in the moving bed has a large effect on the productivity and efficiency of the blast furnace process when operating with low coke rate and using high-reactivity coke. Therefore, an investigation on the effect of the powder's physical properties and the moving bed material on transport phenomena and the accumulation mechanism of powder in the blast furnace is essential.

In the present study, the motion of powder particles was simulated using the discrete element method (DEM), and the effect of the powder particles' shape on the behavior and accumulation of powder was investigated. The study used DEM to reproduce the movement of particles by solving the equations of motion of individual particles. Since the particles were treated as spherical objects in DEM, contact friction and rolling resistance were implemented to represent the irregular shape of actual powder particles. The calculation results showed that contact friction and rotational resistance affected the static holdup of the powder. The amount of clogging of powder at a bottleneck in the moving bed increased with increasing coefficients of friction and resistance. Moreover, the impact of the flow velocity of the gaseous phase on the accumulation behavior of powder was examined. The frictional force on powder particles at the bottleneck increased with an increase in the gas velocity. The clogging of powder occurred easily as a result.

dx.doi.org/10.2355/isijinternational.55.1313

Fabrication of Self-Ordered Porous Alumina via Etidronic Acid Anodizing and Structural Color Generation from Submicrometer-Scale Dimple Array

T. Kikuchi, O. Nishinaga, S. Natsui and R. O. Suzuki

Electrochimica Acta, **156**, 235-243 (2015)

Highly ordered anodic porous alumina with a large-scale cell diameter was successfully fabricated via anodizing in a new electrolyte, etidronic acid (1-hydroxyethane-1, 1-diphosphonic acid). High-purity aluminum specimens were anodized in a 0.3 M etidronic acid solution under constant current density and voltage conditions. Etidronic acid anodizing at 210 to 270 V at the appropriate temperature caused the anodic porous alumina to exhibit self-ordering behavior, and periodic nanostructures measuring 530 to 670 nm in cell diameter were fabricated on the aluminum substrate. The self-ordering voltage and the corresponding cell diameter could be increased without burning by systematically increasing the stepwise voltage. Two-step etidronic acid anodizing without nanoimprinting can easily yield the formation of highly ordered anodic porous alumina with a large-scale cell diameter. A submicrometer-scale dimple array fabricated via etidronic acid anodizing and subsequent selective oxide dissolution gave rise to bright structural color with a rainbow distribution.

Porous Aluminum Oxide Formed by Anodizing in Various Electrolyte Species

T. Kikuchi, D. Nakajima, O. Nishinaga, S. Natsui and R. O. Suzuki

Current Nanoscience, **11**, 560-571 (2015)

Anodizing of aluminum and its alloys is widely investigated and used for corrosion protection, electronic devices, and micro-/nanostructure fabrication. Anodizing of aluminum in acidic solutions causes formation of porous aluminum oxide films, which consists of numerous hexagonal cells perpendicular to the aluminum substrate, and each cell has nanoscale pores at its center. Recently, highly ordered porous aluminum oxide has been widely investigated for various novel nanoapplications. In this review article, we introduce the fundamentals of anodic oxide films including barrier and porous oxides. Then, we summarize the electrolyte species used so far for porous oxide fabrication and describe the self-ordering conditions during anodizing in these electrolyte solutions. Fabrication of highly ordered porous oxides through the vertical section can be achieved by a two-step anodizing and nanoimprint technique. Various nanoapplications based on the ordered porous oxide are also introduced.

Niobium Powder Synthesized by Calciothermic Reduction of Niobium Hydroxide for Use in Capacitors

M. Baba, T. Kikuchi and R. O. Suzuki

Journal of Physics and Chemistry of Solids, **78**, 101-109 (2015)

Metallic niobium powder was produced for applications in electric capacitors via calciothermic reduction of niobium hydroxide in molten $CaCl_2$. Sub-micrometer spherical metallic particles with coral-like morphologies reflected the particle size of the starting oxide powder. A fine powder was obtained from the mixtures of niobium hydroxide and CaO or $Ca(OH)_2$, respectively. Sintered pellets of the metallic powder showed a higher capacitance (CV) than those of the simply reduced powder without pre-treatment, because the shrinkage during sintering was smaller. The CV was as large as that of commercially sintered pellets for tantalum capacitors. Therefore, this niobium powder would act as a higher-voltage capacitor by applying chemical anodic treatment at higher voltages, and a lower oxygen content in the reduced power could realize a lower leak current.

dx.doi.org/10.1016/j.jpcs.2014.11.014

Solubilitiy of Gaseous Carbon Dioxide in Molten LiCl-Li_2O

T. Wakamatsu, T. Uchiyama, S. Natsui, T. Kikuchi and R. O. Suzuki

Fluid Phase Equilibria, **385**, 48-53 (2015)

Carbonate ions in LiCl-Li_2O salt are a source of carbon contamination in the electrolytic refining of metal oxides, and their concentration is also an essential information for understanding the CO_2 decomposition process. In this study, the solubility of gaseous CO_2 in molten LiCl-Li_2O was studied with the goal of developing processes to decompose the oxides effectively. Ar-CO_2 gas mixtures were dissolved in molten salts containing various amounts of Li_2O, and the solubility of the CO_2 gas was calculated by measuring the mass difference between the molten salts before and after the CO_2 dissolution. The molar amount of dissolved CO_2 gas was almost as large as the molar quantity of Li_2O when the partial pressure of CO_2 was 1.0 or 0.5 atm for Li_2O concentrations in the range of 0-60 mol%. This confirms that a large quantity of the oxide ions reacted with the CO_2 gas, resulting in the generation of carbonate ions.

dx.doi.org/10.1016/j.fluid.2014.10.046

Simulation Analysis of Tilted Polyhedron-Shaped Thermoelectric Elements

X.-N. Meng and R. O. Suzuki

J. Electr. Mater., **44**(6), 1469-1476 (2015)

The TE performance of the modules consisting of these polyhedron elements is numerically simulated by using the finite-volume method. The output power, voltage, and current of the polyhedral TE module are greater than those of the parallelogram-element module. The polyhedron shape positively affects heat transfer and the flow of electric charges in the light of increasing the efficiency of conversion from heat to electricity. By varying the shape of the truncated portions, we determine the optimal shape that enables homogeneous heat flux distribution and slow diffusion of thermal energy to obtain the better efficiency of conversion of heat into electricity.
dx.doi.org/10.1007/s11664-014-3418-5

Dimensional Analysis of Thermoelectric Modules under a Constant Heat Flux

R. O. Suzuki, T. Fujisaka, K. O. Ito, X. Meng and H.-T. Sui

J. Electr. Mater., **44**(1), 348-355 (2015)

Thermoelectric power generation is examined in the case of radiative heating. A constant heat flux is assumed in addition to consideration of the Seebeck effect, Peltier effect, and Joule heating with temperature-dependent material properties. Numerical evaluations are conducted using a combination of the finite-volume method and an original simultaneous solver for the heat transfer, thermoelectric, and electric transportation phenomena. Comparison with experimental results shows that the new solver could work well in the numerical calculations. The Seebeck effect becomes larger for longer thermoelectric elements because of the larger temperature difference. The heat transfer to the cold surface is critical to determine the junction temperatures under a constant heat flux from the hot surface. The negative contribution from Peltier cooling and heating can be minimized when the current is smaller for longer elements. A thicker TE module can generate more electric power even under a constant heat flux.

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Transition of the Corrosion Protection Mechanism of Iron Partially Covered with Zinc Coating

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The coupling current map of a Fe specimen partially covered with Zn coating was traced in an atmospheric corrosion test by using a 100-channel electrodes coupling current measurement system. The time series of the coupling current map of the iron surface in an arrangement of a 10 × 10 matrix clearly revealed transition of the corrosion protection mechanism of Fe from sacrificial protection by anodic dissolution of Zn to inhibitory protection by the Zn corrosion product covering the Fe surface. Corrosion products on each electrode were also identified by using microscopic Raman spectroscopy. In the sacrificial protection period, Zn ions extended to the area around the Zn-coating and formed a hydrozincite layer due to absorption of CO_2 in the solution alkalized by the cathodic oxygen reduction. After complete depletion of the Zn coating, corrosion of Fe could be inhibited by the hydrozincite and simonkolleite layer covering the Fe surface but not by the zincite layer.

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Promotion of α-Al_2O_3 Formation on an Ni-Al Alloy Using a Ni-Fe_2O_3 Nano-Composite Seeding Layer

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Surface and Coatings Technology, **266**, 113-121(2015).

Thin seeding layers of Ni and Ni–Fe_2O_3 composites were successfully formed on an $Ni_{50}Al$ alloy using the pulse electrodeposition method (PED) from a Watts bath in order to promote α-Al_2O_3 formation for improving the high temperature oxidation resistance of the $Ni_{50}Al$ alloy. The conditions for the PED and the effects of these seeding layers on Al_2O_3 scale formation on the $Ni_{50}Al$ alloy were investigated. The coated samples showed thicker oxide scales than bare $Ni_{50}Al$ samples in oxidation tests at 1000 °C in air. At the initial stage of oxidation (1 h), a single layer scale composed of blade-like crystals of metastable θ-Al_2O_3 was formed. The oxide scales formed on the PED coated samples had a multilayered structure consisting of an inner layer of either a mixture of θ-Al_2O_3 and α-Al_2O_3 or of single-phase α-Al_2O_3, intermediate $NiAl_2O_4$ layer and an outer NiO layer. The Ni- seeding layer was found to delay the phase transformation of θ-Al_2O_3 to α-Al_2O_3 to 100 h of oxidation. Addition of 3.1% Fe_2O_3 to the Ni-seeding layer accelerated the transformation of θ-Al_2O_3 to α-Al_2O_3 after 9 h of oxidation. Further addition of Fe_2O_3 nano-powder (5.2 %–7.4 %) to the Ni-seeding layer successfully suppressed the θ-Al_2O_3 formation even at 1 h of oxidation. The Al_2O_3 phase structure and thickness of the oxide scales were found to be considerably affected by these seeding layers via two main factors: (i) formation of $NiAl_2O_4$ and (ii) the effect of Fe_2O_3 to accelerate the transformation of metastable Al_2O_3 to stable α-Al_2O_3 or to suppress the formation of metastable Al_2O_3.

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Coupling current mapping of corroding iron in a wet and dry cyclic corrosion test

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Abstract A specimen composed of 100 iron wire electrodes in a 10×10 array was exposed to a wet and dry cycling corrosion test with a drop of sodium chloride solution to investigate the spatial distribution of coupling current and anodic/cathodic coupling charge during the progress of corrosion on an iron surface. A bare specimen showed transition of a coupling current map depending on the relative humidity in a short time span and transition from the induction, progress, and inhibition of corrosion due to rust accumulation on the surface in a long time span. The coupling current map con- firmed that major coupling occurred between neighboring electrodes due to the limitation of ionic path length on the specimen in an atmospheric corrosion condition. An electric charge map calculated from integration of the anodic coupling current corresponded qualitatively to the actual accumulation of rust on the specimen surface. The specimen coated with acrylic paint showed formation of coupling between electrodes under the paint before paint breaching and successive progress of the coupling distribution around the breaching point. When a scratch was made in the paint, progress of the coupling distribution along the scratch was observed.

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Effect of Hydrogen Sulfide Ions on the Passive Behavior of Type 316L Stainless Steel

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J. Electrochem. Soc., **162**(14), C685-C692 (2015).

The effect of hydrogen sulfide ions (HS^-) on the passivity of type 316L stainless steel was investigated in pH 8.4 boric acid-borate buffer solution. Galvanostatic polarization of a silver microelectrode covered with Ag_2S generated both OH^- and HS^- above the stainless steel surface. During potentiostatic polarization of the stainless steel, the passivity-maintaining current density increased with increase in the concentration of HS^- in the vicinity of the surface. The impedance of the stainless steel at a constant frequency decreased during polarization in the presence of HS^-, while it was sustained after dilution of HS^-. Electrochemical impedance spectroscopy (EIS), Mott-Schottky (M-S) analysis and scanning electrochemical microscopy (SECM) showed that a defective and n-type semiconductive passive film was formed in the solution containing HS^-. Auger electron spectroscopy (AES) revealed that metal cations and oxygen vacancies in the passive film on the stainless steel increased when it was formed in a HS^- containing solution. The series of changes in passive film properties is thought to be due to adsorption of HS^- on the film surface during the polarization.

Microelectrochemistry in the Heat-Tinted Zone of a Stainless Steel Weldment

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Zairyo-to-Kankyo, **64** (12), 551-557 (2015).

The deterioration mechanism of corrosion resistance in the heat-tinted zone of a stainless steel weldment was studied. Local electrochemical measurements with a microcapillary cell and surface analyses in small regions were conducted to correlate local variation in corrosion behavior and surface structure. Depletion in Cr content at the substrate surface and formation of a Fe-rich oxide layer on the surface were confirmed, although their distances from the welding bead were not identical. It was also revealed that the corrosion behaviors in the area with Cr depletion and the area with the Fe-rich oxide layer were different. The Cr depletion led to a lowering in the pitting potential due to the activation of substrate steel, whereas the Fe-rich oxide layer led to preferential rusting in the cyclic corrosion test due to deterioration of the surface protective layer.

Passivity of Dual-Phase Carbon Steel with Ferrite and Martensite Phases in pH 8.4 Boric Acid-Borate Buffer Solution

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J. Electrochem. Soc., **162**(7), C322-C326 (2015).

Passivity of a dual-phase carbon steel with ferrite and martensite phases was investigated in pH 8.4 boric acid-borate buffer solution. The corrosion potential of the dual-phase steel was higher than that of pure martensitic steel and lower than that of pure ferritic steel. In dynamic polarization measurements, the passivity-maintaining current of the dual-phase steel was an intermediate value of those of pure ferritic and martensitic steels. EIS revealed that both the charge transfer resistance and capacitance of the oxide film formed on the dual-phase steel were intermediate between those of pure ferritic and martensitic steels. Although the donor density in the oxide film of the dual-phase steel was similar to that of pure ferritic steel, it was smaller than that of pure martensitic steel. SECM showed that the passive film formed on the martensite phase of the dual-phase steel had better electronic conductivity than that of the passive film formed on the ferrite phase. These differences in local passivity of the dual-phase steel suggested that the passive film formed on the ferrite phase has better passivity but larger scattering of the property than that of the passive film on the martensite phase. The local passivity of the dual-phase steel was strongly dependent on the texture of the substrate material.

Development of a Liquid-Phase Ion Gun and Its Application for Sulfidation of Silver Surface

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J. Electrochem. Soc., **162**(4), C115-C120 (2015).

A system for safe generation of sulfide ions was established by using the microelectrode technique in order to investigate sulfidation of the metal surface of silver. Both silver microelectrode sulfidation and silver sulfide reduction on the microelectrode were reversible in Na_2S solution and corresponded to Ag_2S formation and HS^- generation, respectively. Cathodic polarization of Ag_2S, which covered the silver microelectrode, in pH 8.4 boric-borate buffer solution successfully generated HS^- above a glass or silver substrate. Concentration of HS^- in the vicinity of the substrate was dependent on the distance between the microelectrode and the substrate. The silver substrate was locally sulfidated by HS^- generated from the microelectrode. However, at potentials higher than 0.14 V_{RHE}, local sulfidation of the silver substrate was independent of the substrate potential. It is thought that mass transport of HS^- is dominant for sulfidation of the silver substrate.

Corrosion Performance and Surface Analysis of Ti-Ni-Pd-Ru-Cr alloy in Nitric Acid Solution

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Corrosion Science, **91**, 120-128 (2015)

The corrosion resistance of Ti–0.4Ni–0.015Pd–0.025Ru–0.14Cr (AKOT Ti) and commercially pure titanium (CP Ti) has been studied in different concentrations of 6, 9 and 11.5M HNO_3, and boiling 15.65 M HNO_3. In both CP Ti and AKOT Ti alloy, the open circuit potential and corrosion potential are shifted to more noble potential with increasing concentrations. However, passive current density decreases with increasing concentration. Lower corrosion rate was observed in AKOT Ti (~ 0.075 mm/ y) compared to CP Ti (~ 0.22 mm/y) in boiling 15.65 M HNO_3 after 240 h. The mechanisms by which dissolved titanium ions affect the corrosion are also discussed.

Corrosion degradation of AISI type 304L stainless steel for application in nuclear reprocessing plant

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Journal of Solid State Electrochemistry, **19**, 3533-3542 (2015)

The degradation of materials involving corrosion in handling nitric acid in the spent fuel nuclear reprocessing plant is a serious issue. In the present work, the corrosion resistance of American Iron and Steel Institute (AISI) type 304L stain- less steel (SS) and nitric acid grade (NAG) type 310L SS in 1 to 11.5 M HNO_3 and boiling 15.65 M HNO_3 was evaluated. In both the alloy steels, the open circuit potential and corrosion potential are shifted to more noble potential with increasing concentrations. However, the passive current density was not affected, and the transpassive potential was shifted to higher potential with increasing concentrations. The corrosion rate measured in boiling 15.65 M HNO_3 after 240 h shows a much lower corrosion rate in type 310L SS (~0.06 ± 0.012 mm/y) then type 304L SS (~ 0.18 ± 0.02–0.2 ± 0.001 mm/y). These observations are corroborated with the scanning electron microscope (SEM) morphologies that show severe intergranular corrosion (IGC) attack in type 304L SS then in type 310L SS. The X-ray photoelectron spectroscopy (XPS) study of the passive oxide films of both alloy steels shows the presence of Cr_2O_3 and SiO_2, and the depth profile indicated predominant Si enrichment.

Surface analysis of passive films formed on Aluminum alloys in different metal cation containing solutions

M. Sakairi, R. Sasaki, K. Suzuki, and A. Kaneko

Proc. of Eurcorr 2015, paper No. 492, (2015)

The effect of metal cations on the characteristics of passive films formed on aluminum alloys during immersion in neutral solutions with different metal cations was investigated. The surface observation showed that surface morphology was strongly affected by the kind of metal cations. The XPS analysis showed that the thickness of the passive film formed on A3003 was thinner than that on A5052, and hard metal cations were incorporated into the passive films.

Resent research progress in creation of hydrogen-passive surfaces on steels to prevent of hydrogen embrittlement

M. Sakairi

Proc. of Asia Steel 2015, 538-539 (2015)

A reduction in susceptibility to hydrogen embrittlement of high strength steels has become an important issue to ensure reliability and safety in the practical use of the steels. One idea to mitigate hydrogen embrittlement based on surface reactions is to create surfaces preventing entry of hydrogen into the steels, hydrogen-passive surfaces. To elucidate detail of the hydrogen entry process considering the properties of surfaces and interfaces is essential for achieving the creation of hydrogen-passive surfaces. Research grope to investigate the hydrogen entry process focused on properties of surfaces and surface reaction is working in The Iron and Steel Institute of Japan. The resent research progress of the grope is introduced.

Area selected electrochemical corrosion tests

M. Sakairi

Zairyo-to-Kankyo, **64**, 66-72 (2015)

An area selected electrochemical corrosion tests, which are used a focusing pulse YAG laser beam irradiation (laser machining) technique and micro-electrochemical cell techniques, were applied to investigate the re-passivation kinetics of metals, corrosion behavior of coated steels and hydrogen entry behavior of coated steels. In this paper, the application of the techniques for evaluation of post welded heat treatment on electrochemical behavior of low C-13%Cr welded joints, re-passivation behavior of titanium in artificial saliva, detection of atmospheric corrosion generated hydrogen and hydrogen permeation efficiency at scratched areas are described. (Japanese)

Investigation of corrosion behavior with laser irradiation and electrochemical techniques

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Journal of The Surface Science Society of Japan, **36**, 41-46 (2015)

A focusing pulse YAG laser beam irradiation (laser machining) technique and micro-electrochemical cell technique were applied to investigate the corrosion behavior of coated steels. These techniques make it possible to investigate the corrosion behavior with control of areas and shapes. In this paper, the application of the techniques for atmospheric corrosion behavior of size controlled model scratches formed on coated steels, detection of atmospheric corrosion generated hydrogen and hydrogen permeation efficiency at scratched areas are described.

Surface Analysis of Al Alloys with X-Ray Photoelectron and Auger Electron Spectroscopy

M. Sakairi

Zairyo-to-Kankyo, **64**, 281-284 (2015)

In this paper, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were applied to investigate passive films formed on aluminum alloy in 0.5 kmol m^{-3} H_3BO_3 / 0.05 kmol m^{-3} $Na_2B_4O_7$ with different metal cations. The metal cation is classified by metal cation hardness, X, which are calculated based on the concept of hard and soft acids and bases (HSAB) of the acid and base in Lewis's rule. From XPS analysis, the metal cations with $X > 4$ were incorporated in passive films. The area-selected surface analysis of AES was also introduced.