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## **CURRENT ACTIVITIES and PRESENTATIONS**



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Our research activities are concerned with molten salts electrolysis and surface sciences about metal surface.

Research programs in progress are as follows:

(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 selected NaTFSI-TEATFSI ionic liquid as candidate of the electrolytic melt. In the electrorefining experiment, more than 99.9% pure Na was obtained from simulated Na in used Na-S battery.

(2) Electrodeposition of Zr in chloride-fluoride molten salt

Metallic Zr was electrodeposited on Cu substrate in LiCl-KCl-LiF molten salt containing ZrF<sub>4</sub> at 973 K. In voltammogram, cathodic current which corresponds to

reduction reactions of  $\text{Zr(IV)} + 2e \rightarrow \text{Zr(II)}$  and  $\text{Zr(II)} + 2e \rightarrow \text{Zr(0)}$  were flowed at -1.4 and -1.6 V vs.  $\text{Ag/Ag}^+$ , respectively. The electrodeposition was performed by constant potential electrolysis from -1.4 to -1.6 V. The Zr was electrodeposited as a  $\text{Cu}_{10}\text{Zr}_7$  and  $\text{CuZr}$  on Cu substrate at -1.6 V.

(3) Development of functional glass by ion-exchange reaction in molten salt

Glass plates were immersed in a molten salt of  $\text{KNO}_3\text{-AgNO}_3$  at 698 K. During the immersion, ion-exchange was induced at the surface of the glass. By the reduction of the glass, Ag ion changed to metallic Ag.

(4) Development of Al- $\text{Cl}_2$  cell in ionic liquid

A fuel cell which consists of dissolution reaction of Al and reduction reaction of  $\text{Cl}_2$  gas was arranged in 1-Ethyl-3-methylimidazolium chloride(EMIC) - $\text{AlCl}_3$  ionic liquid at 303 K. The open circuit voltage of the cell was about 2.3 V. The cell voltage changed to 1.5 V with current density of  $14 \text{ mAcm}^{-2}$ . When the circuit was open, cell voltage quickly recovered to 2.3 V.

(5) Development of efficient PEFC cathode for oxygen reduction reaction (ORR)

Oxygen reduction reaction (ORR) was studied on Pd electrodes. The Pd electrode did not reveal a high ORR current and when it was covered by mono-atomic layers of Pt, however, the ORR current compared to that of Pt electrode.

The ORR current was also examined by a co-deposition layer of Co and Pt on carbon electrode. Co was firstly electrodeposited on the electrode and then the electrodes was immersed in the acidic solution containing Pt ions. The Co layer was replaced with Pt in atomic level. The surface layers containing Co and Pt thus formed exhibits a relative high ORR current.

(6) Investigation of Li metal surface by in situ Raman spectroscopy

Li metals in some non-aqueous solution were evaluated by Raman spectrometer. Some compounds by oxidized of Li were identified.



## Other Activities

Prof. Ohtsuka attended PRiME2012, Honolulu, USA, Oct. 7-12 2012 and presented a paper entitled by " The effect of Sulfate and Chloride Ions on the Rust Composition of Weathering Steel".

Assoc. Prof. Ueda attended the 4th Asian Conference on Molten Salt Chemistry and Technology, Matsushima, Japan, September 23-27, PRiME2012, Honolulu, USA, Oct. 7-12, and Interfinish 2012, Milano, November 13-16, 2012 and presented papers entitled by " Electrodeposition of Al Alloys as a Lubricating Material in Molten Salt", "Al-Pt alloy deposition in  $\text{AlCl}_3$ -NaCl-KCl molten salt", and " Surface finishing of Mg alloy by Al electroplating".

Asist. Prof. Hyono attended PRiME2012, Honolulu, USA, Oct. 7-12, 2012 and presented a paper entitled by" Oxygen Reduction on Pt-Pd Electrode for PEFC Cathode".

## Presentations

M. Abe, A. Hyono, M. Ueda, T. Ohtsuka, Semiconducting properties of Fe-Cr alloys varying concentration of Cr, Winter Meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 19-20, 2012

M. Koya, T. Ohtsuka, A. Tahara, Evaluation of rust on steel by surface roughness measurements, Winter meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 19-20, 2012

K. Yoshida, M. Ueda, T. Ohtsuka, Anodic reaction on BDD electrode in LiOH -LiCl molten salt, Winter meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 19-20, 2012

K. Honda, M. Ueda, Toshiaki Ohtsuka, Electrorefining of Na using pool Na electrodes in ionic liquid, Winter meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 19-20, 2012

W. Murakami, M. Ueda, T. Ohtsuka, Development of Zn-Mg alloy coated steel sheets by vapor deposition and evaluation of their corrosion resistance, Winter meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 19-20, 2012

T. Ohtsuka, Corrosion products of Zinc and corrosion resistance mechanism, The 284th meeting of corrosion committee in The Society of Materials Science, Jpn, Osaka, January 24, 2012

S. Hariyama, M. Ueda, T. Ohtsuka, Al electroplating on Mg alloy in ionic liquid containing additives, 125th spring meeting of Surface finishing society of Jpn, Tokyo City University, Tokyo, March, 13-14, 2012

T. Ohtsuka, M. Koya, In-situ Raman spectroscopy of rust on weathering steel during the reduction, The 163th spring meeting of ISIJ, Yokohama national University, Yokohama, March 28-30, 2012

T. Ohtsuka, M. Koya, A. Tahara, M. Miura, Evaluation of steel rust layer by measurement of their surface roughness and particle size, The 163th Spring meeting of ISIJ, Yokohama national University, Yokohama, March 28-30, 2012

M. Abe, A. Hyono, M. Ueda, T. Ohtsuka, T. Ishii, Relationship between impurity concentration and characteristics of passive film on ferritic stainless steel, The 150th Spring meeting of the Japan institute of metals, Yokohama National University, Yokohama, March 29, 2012

T. Ohtsuka, Electrochemical and optical studies on corrosion protection of metallic materials Spring meeting of ECSJ 2012, Hamamatsu, March 29-31, 2012

Mu Li, A. Hyono, M. Ueda, T. Ohtsuka, Preparation of Pt-Co alloy catalysis on glassy carbon electrode by electroreduction for oxygen reduction reaction, Spring meeting of ECSJ 2012, Hamamatsu, March 29-31, 2012

M. Sasaki, A. Hyono, M. Ueda, T. Ohtsuka, Preparation of PPy film doped various poly-acids on steel surface, Spring meeting of ECSJ 2012, Hamamatsu, March 29-31, 2012

K. Yoshida, M. Ueda, T. Ohtsuka, Oxygen evolution reaction on BDD electrode in LiOH-LiCl molten salt, Spring meeting of ECSJ 2012, Hamamatsu, March 29-31, 2012

Y. Hamaguchi, A. Hyono, T. Ohtsuka, M. Sakairi, K. Fushimi, G. Nakayama, Y. Sakakibara, Surface oxide film on Ni based alloys exposed to PWR environment, Materials and environments 2012, Waseda University, Tokyo, April 25-27, 2012

T. Ohtsuka, Change in composition of rusts on weathering steel with anions, NIMS Conference 2012, Tsukuba, June 4-6, 2012

R. Inaba, K. Honda, M. Ueda, T. Ohtsuka, Comparison of TEATFSI and TBATFSI as an electrolyte in electrorefining of metallic sodium, 22nd annual seminar of electrode materials, Yamanashi University, Kofu, July 27, 2012

T. Ohtsuka, Science of steel rust and corrosion resistance by rust layer, Summer meeting of Hokkaido Branch of Surface finishing society Jpn and Corrosion engineering of Jpn, Muroran Institute of Technology, Muroran, July 27, 2012,

K. Kurauchi, T. Kurauchi, T. Nakanishi, K. Fushimi, Y. Hasegawa, T. Ohtsuka, In-situ polarized reflectance imaging of titanium passive film, Annual meeting on photochemistry 2012, Tokyo Institute of Technology, Tokyo, September 12-14, 2012

T. Ohtsuka, Passivation and corrosion protection of steel surface by conductive PPy coating, 164th Fall meeting of ISIJ, Matsuyama University, Matsuyama, September 17-19, 2012.

K. Yoshida, M. Ueda, T. Ohtsuka, Electrowinning of Li from LiOH by BDD anode and tungsten cathode, 44th Symposium on Molten Salt Chemistry, Hotel Taikanso, Matsushima, September 23-27, 2012

Y. Sakai, M. Ueda, T. Ohtsuka, Formation of Ag alloy particles in the glass by ion exchange treatment in molten salt, 44th Symposium on Molten Salt Chemistry, Hotel Taikanso, Matsushima, September 23-27, 2012

M. Ueda, Electrodeposition of Al Alloys as a Lubricating Material in Molten Salt, 4th Asian Conference on Molten Salt Chemistry and Technology, Hotel Taikanso, Matsushima, September 23-27, 2012

K. Kurauchi, K. Fushimi, T. Nakanishi, Y. Hasegawa, T. Ohtsuka, In-situ observation of titanium passive film by polarized reflectance imaging, The 59th symposium on materials and environment, Asahikawa crystal hall, Asahikawa, September 24-26, 2012

S. Nan, M. Ueda, T. Ohtsuka, Corrosion prevention of zinc coated AZ91D alloy by bi-layered polypyrrole film, The 59th symposium on materials and environment, Asahikawa crystal hall, Asahikawa, September 24-26, 2012

L. Yanhua, A. Hyono, M. Ueda, T. Ohtsuka, Electrochemical synthesis of Polypyrrole films from phytate solution for corrosion protection on copper, The 59th symposium on materials and environment, Asahikawa crystal hall, Asahikawa, September 24-26, 2012

M. Sasaki, A. Hyono, M. Ueda, and T. Ohtsuka, Corrosion protection of steel by conducting polypyrrole film doped with various poly-acids, 126th annual meeting of Surface finishing society of Jpn, Muroran institute of technology, Muroran, September 27-28, 2012

T. Ohtsuka, Corrosion protection of steels and analysis of surface inclusion by AES measurement, 2012 JEOL EPMA surface analysis meeting, University of Tokyo, Tokyo, October. 4-5 2012

A. Hyono, Y. Sugawara, M. Ueda, and T. Ohtsuka, Oxygen Reduction on Pt-Pd Electrode for PEFC Cathod, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

R. Inaba, M. Ueda, and T. Ohtsuka, Evaluation of NaTFSI-TBATFSI Ionic Liquid as an Electrolytic Melt for Na Electrorefining, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

T. Ohtsuka, S. Tanaka, M. Koya, A. Hyono, and M. Ueda, The effect of Sulfate and Chloride Ions on the Rust Composition of Weathering Steel, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

M. Abe, A. Hyono, M. Ueda, T. Ohtsuka, and T. Ishii, The effect on Impurities of the Properties of Passive Oxides on Stainless Steels, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

Y. Hamaguchi and T. Ohtsuka, Effect of Stress on Oxide Film Growth on SUS 316L Stainless Steel under High Pressure-High Temperature Water, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

M. Sasaki, A. Hyono, M. Ueda, and T. Ohtsuka, Corrosion Protection of Steel by Conducting Polypyrrole Film Doped with Poly-acids of Mo and W, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

M. Ueda, H. Hayashi, and T. Ohtsuka, Al-Pt alloy deposition in  $\text{AlCl}_3$ -NaCl-KCl molten salt, PRiME2012, Hawaii Convention Center and the Hilton Hawaiian Village, Honolulu, USA, Oct. 7-12, 2012

T. Ohtsuka, Latest Advance and Future Perspective on Structure of Iron Rust and Mechanisms of Corrosion Protection, The 211th Nishiyama Memorial Symposium-Advances and Future Perspectives in Corrosion Science of Metals, Tokyo, November. 9, 2012

M. Ueda, S. Hariyama, T. Ohtsuka, Surface finishing of Mg alloy by Al electroplating, Interfinish 2012, Politecnico di Milano, Milano, November 13-16

T. Ohtsuka, Latest Advance and Future Perspective on Structure of Iron Rust and Mechanisms of Corrosion Protection, The 212th Nishiyama Memorial Symposium- Advances and Future Perspectives in Corrosion Science of Metals, Osaka, November. 16, 2012

M. Ueda, S. Hariyama, Y. Tabei, and T. Ohtsuka, Al electroplating on Mg alloys in an ionic liquid for corrosion protection, 2012 International Joint Symposium between Hokkaido University and Chungnan National University on Advanced Materials Science & Engineering, Hokkaido University, Sapporo, November 29-December 1, 2012

Y. Hamaguchi and T. Ohtsuka, Effect of stress and dissolved oxygen concentration on oxide film growth on SUS316L stainless steel under high pressure-high temperature water, 2012 International Joint Symposium between Hokkaido University and Chungnan National University on Advanced Materials Science & Engineering, Hokkaido University, Sapporo, November 29-December 1, 2012

M. Sasaki, A. Hyono, M. Ueda, and T. Ohtsuka, Evaluatio of corrosion protection of steel covered with conducting polypyrrole doped with heteropoly molybdate ions, 2012 International Joint Symposium between Hokkaido University and Chungnan National University on Advanced Materials Science & Engineering, Hokkaido University, Sapporo, November 29-December 1, 2012

Y. Lei, A. Hyono, M. Ueda, and T. Ohtsuka, Electrochemical synthesis of polypyrrole films for corrosion protection of copper, 2012 International Joint Symposium between Hokkaido University and Chungnan National University on Advanced Materials Science & Engineering, Hokkaido University, Sapporo, November 29-December 1, 2012

T. Ohtsuka, Observation of surface inclusions by AES and the potential for the corrosion study, 4th joint symposium on corrosion in Hokkaido University and NIMS, NIMS, Tsukuba, December 4, 2012

M. Abe, A. Hyono, M. Ueda, T. Ohtsuka, Corrosion study concerning with inclusions using Auger electron spectroscopy, Corrosion dream 2012, Osaka University, Osaka, December 7, 2012

T. Ohtsuka, Corrosion protection of steel by conductive PPy coating, Special lecture of Hokkaido Branch of Surface finishing Society of Jpn, Hokkaido University, Sapporo, December 12, 2012

## 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

Potential Modulation Reflectance: Wavelength region from 350 to 800 nm

Raman Scattering Spectrometer: Bonko 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

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

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Associated Professor Yoshitaka, who visited RWTH Aachen University as a Humboldt research fellowship, came back to our lab in April 2012. Assistant Professor Etsushi Tsuji visited Corrosion and Protection Centre, School of Materials, the University of Manchester for 2 months from July 2012 for collaborative research with Prof. George E. Thompson and Prof. Peter Skeldon. Ms Ye Su, a master course student of the University of Science and Technology Beijing, China, stay from October 2011 to September 2012 as an exchange foreign student.

The research activities of the laboratory are directed towards the development of advanced oxide films and nanomaterials utilizing anodic oxidation process and sol-gel process. 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 as follows:

(1) Intermediate-temperature fuel cells

We successfully fabricated gas-tight silicate and phosphate nanofilms, which show efficient proton conductivity even in dry atmosphere at intermediate temperatures (200-400°C). Utilizing the proton-conducting nanofilms as an electrolyte membrane, we designed a hydrogen membrane fuel cells (HMFCs). In HMFCs, palladium foil was used as a hydrogen-permeable anode and we succeeded power generation. We also found that the  $ZrO_2-WO_3-SiO_2$  films formed by anodizing of magnetron-sputtered Zr-W-Si alloys reveal high proton conductivity even below 200°C.

(2) Tailoring of self-organized porous anodic oxides on various metals

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. We have already successfully developed self-organized porous anodic films on titanium, niobium and aluminum in the hot phosphate-glycerol electrolyte. In addition, using organic electrolytes containing fluoride ions, self-organized nanoporous anodic films have been successfully developed on iron and stainless steel. The growth behavior and their properties have been examined in detail.

(3) Formation of barrier-type anodic oxide films on zirconium and titanium alloys for capacitor application

Novel anodic oxide films with excellent dielectric properties have been tailored on non-equilibrium, single phase zirconium, niobium and titanium alloys for replacing the currently used tantalum solid capacitors. Structural modification of the anodic films by incorporation of alloying elements is a key issue to improve the dielectric properties. Recently, we found that nanocomposite anodic oxide films with high capacitance have been formed by anodizing of Zr-Si and Zr-Al alloys. The oxide films consist of nanocrystalline tetragonal  $ZrO_2$  phase and amorphous matrix and the former contributes to the enhancement of permittivity and the latter is responsible for the reduction of film thickness.

(4) 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 superoleophobic surfaces after coating with a fluoroalkyl monolayer, which had the lowest surface energy.

(5) Spark anodizing for development of thick oxide films with excellent wear and corrosion resistance

Spark anodizing of titanium alloys has been performed to form hard and adhesive oxide ceramic coating to improve the wear resistance of various titanium alloys. Similar coatings with high hardness have been developed on Ti, Ti-6Al-4V and Ti-15V-3Al-3Cr-3Sn. However, the adhesion of the coating developed on Ti-15V-3Al-3Cr-3Sn was relatively poor. The poor adhesion was associated with void formation in the inner layer close to the alloy/film interface. We found two-step spark anodizing improve markedly the adhesion of the coating without degradation of high wear resistance.

(6) Surface characterization using glow discharge optical emission spectroscopy

Radio frequency glow discharge optical emission spectroscopy (rf-GDOES) with excellent depth resolution of sub-nanometer scale has been used to analyze thin anodic films as well as passive films. The excellent depth resolution even for non-conducting layers and extremely high sputtering rate allow obtaining depth profiles precisely and quantitatively. Depth profiles of a range of thin and porous anodic oxide films were successfully analyzed at high depth resolution.

#### Other Activities

Prof. H. Habazaki presented keynote lectures at the 63rd Annual Meeting of International Society of Electrochemistry, which was held on 19-24 August 2012 at Clarion Congress Hotel, Plague and at PRiME2012, which was held on 7-12 October 2012 at Hilton Hawaiian Village & Hawaii Convention Center, Honolulu. Assoc. Prof. Y. Aoki presented keynote lectures at 13th Asian Conference on Solid State Ionics, which was held on 17-20th Jul. 2012 at Tohoku University, Sendai and at 2nd All Hands Meeting of SFB-917 'Nanoswitches' on 12-14th Sep. 2012, Aachen.

## 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 operating in contact and tapping modes.

Impedance analyzer: Solartron 1260, measureable in the frequency range of 10  $\mu$ Hz 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.

## Presentations

K. Ye, Y. Aoki, E. Tsuji, S. Nagata, H. Habazaki, "Improved Protonic Transport of Anodic ZrO<sub>2</sub>-WO<sub>3</sub> Nanofilms by Silicon Addition into the Zr-W system", 5th GCOE International Symposium/1st International Symposium of Graduate School of Chemical Sciences and Engineering, "Green and Sustainable Chemistry for Next Generation, 22-23 February, Hokkaido University, Sapporo (2012)

T. Fujii, E. Tsuji, Y. Aoki, H. Habazaki, "Important Role of Nanomorphology in Nanometer/Submicrometer Hierarchical Surfaces for Super-Oil-Repellency", 5th GCOE International Symposium/1st International Symposium of Graduate School of Chemical Sciences and Engineering, "Green and Sustainable Chemistry for Next Generation, 22-23 February, Hokkaido University, Sapporo (2012)

S. P. Sah, E. Tsuji, Y. Aoki, H. Habazaki, "Cathodic Pulse Breakdown of Anodic Films of Aluminum—a Fundamental Study for AC Plasma Electrolytic Oxidation", 5th GCOE International Symposium/1st International Symposium of Graduate School of Chemical Sciences and Engineering, "Green and Sustainable Chemistry for Next Generation, 22-23 February, Hokkaido University, Sapporo (2012)

H. Habazaki, Y. Aoki, Y. Ke, D. Kowalski, "Efficient proton-conducting amorphous

oxide nanofilms for intermediate-temperature fuel cells”, International Conference and Workshop on Nanostructured Ceramics and Other Nanomaterials 2012 (ICWNCN2012), 14-15 March, University of Delhi, Delhi, India (2012) (Invited) T. Fujii, H. Sato, E. Tsuji, H. Habazaki, P. Skeldon, G.E. Thompson, “Fabrication of super-liquid-repellent surfaces by anodizing”, 6th International Symposium on Aluminium Surface Science and Technology, 27 -31 May, Hilton Sorrent Palace Hotel, Sorrent, Italy, (2012)

Y. Aoki, H. Habazaki, T. Kunitake and M. Martin “Finite size effect of proton conductivity of amorphous oxide thin films and its application to hydrogen-permeable membrane fuel cell” at Nature Conference “Frontier in Electronic Materials: Correlation Effects and Memristive Phenomena”, 17-20th June, Aachen (2012).

Ke Ye, Yoshitaka Aoki, Etsushi Tsuji, Shinji Nagata, Hiroki Habazaki, “Proton conductivity of anodic  $ZrO_2$ - $WO_3$ - $SiO_2$  nanofilms”, The 13th Asian Conference on Solid State Ionics, 17-20th July, Tohoku University, Sendai (2012)

R. Nonaka, Y. Aoki, E. Tsuji, H. Habazaki, “Hydrogen-permeable membrane fuel cells with amorphous zirconium phosphate thin film electrolyte”, The 13th Asian Conference on Solid State Ionics, 17-20th July, Tohoku University, Sendai (2012)

Y. Aoki and H. Habazaki “Finite size effect of proton conductivity of sol-gel derived amorphous thin films” 13th Asian Conference on Solid State Ionics, 17-20th July, Tohoku University, Sendai (2012) (keynote)

E. Tsuji, Y. Taguchi, H. Habazaki, “Preparation and Photocatalytic Activity of Non-annealed Anatase  $TiO_2$  Mesoporous Film by Anodizing in Hot Phosphate/glycerol Electrolyte”, 9th International Symposium on Electrochemical Micro & Nanosystem Technologies (EMNT2012), 15-17 August, Johannes Kepler University, Linz (2012)

H. Habazaki, K. Kure, Y. Konno, S. Yang, E. Tsuji, Y. Aoki, “Growth of Porous Anodic Films on Metals in Organic Electrolytes” The 63rd Annual Meeting of International Society of Electrochemistry, 19-24 August, Clarion Congress Hotel, Plague (2012) (Keynote)

A. Mozalev, H. Habazaki, M. Sakairi, J. Hubalek, “Formation-structure-properties

of nanocomposite mixed oxide films prepared by porous-alumina-assisted anodizing of Zr-50at.%W alloy layers”, The 63rd Annual Meeting of International Society of Electrochemistry, 19-24 August, Clarion Congress Hotel, Plague (2012)

F. di Quarto, F. di Franco, M. Santamaria, M. Vittoria Diamanti, C. Monarca, H. Habazaki, “Amorphous to Crystalline Transition in Anodic Oxide on Ti and Ti-Si alloys: A Photoelectrochemical Study”, The 63rd Annual Meeting of International Society of Electrochemistry, 19-24 August, Clarion Congress Hotel, Plague (2012)

M. Santamaria, F. Di Quarto, S. Terracina, H. Habazaki, “Photoelectrochemical Characterization of Porous Anodic Films on Iron Grown in Fluoride-containing Ethylene Glycol Electrolyte”, The 63rd Annual Meeting of International Society of Electrochemistry, 19-24 August, Clarion Congress Hotel, Plague (2012)

Y. Aoki, M. Martin, C. Wiemann, V. Feyer, H.-I. Yoo and H.-S. Kim “Switching behavior of highly-nonstoichiometric GaO<sub>x</sub> thin films”, at 2nd All Hands Meeting of SFB-917 'Nanoswitches', 17-19th September, Aachen (2012)

Y. Aoki and H. Habazaki “Finite size effect of proton conductivity of sol-gel derived amorphous aluminosilicate thin films” 16th Conference on Solid State Proton Conductor, 10-14th September, MINATEC, Grenoble (2012)

H. Habazaki, T. Fujii, E. Tsuji, “Importance of Pore Morphology for Super-Liquid Repellency of Solid Surfaces”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center, Honolulu (2012) (Keynote)

H. Satoh, T. Fujii, E. Tsuji, and H. Habazaki, “Study on the Formation of Self-Assembled Monolayers on Anodized Aluminum”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center, Honolulu (2012)

S. Yang, Y. Konno, E. Tuji, Y. Aoki, H. Shoji, P. Skeldon, G. E. Thompson, H. Habazaki, “Formation of Self-Organized Nanoporous Anodic Films on Carbon Steels”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center, Honolulu (2012)

E. Tsuji, N. Hirata, and H. Habazaki, “Preparation of Non-annealed Anatase TiO<sub>2</sub> Films on ITO substrates by Anodizing in Hot Phosphate/glycerol”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center,

## Honolulu (2012)

S. Ahn, J. Yang, H. Kim, H. Habazaki, S. Park, “The Electrochemical Behavior of CNFs by Liquid Phase Carbonization Using Polyethylene Oxide(PEO)”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center, Honolulu (2012)

M. Ishizuka, E. Tsuji, Y. Aoki, H. Habazaki, “Capacitance Enhancement of Anodic ZrO<sub>2</sub> Films by Simultaneous Incorporation of Silicon and Yttrium Species”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center, Honolulu (2012)

K. Ye, Y. Aoki, E. Tsuji, S. Nagata, H. Habazaki, “Enhanced Proton Conductivity by Hydrogenation in Anodic ZrO<sub>2</sub>-WO<sub>3</sub>-SiO<sub>2</sub> Nanofilms”, PRiME2012, 7-12 October 2012, Hilton Hawaiian Village & Hawaii Convention Center, Honolulu (2012)

N. Hirata, E. Tsuji, Y. Aoki, H. Habazaki, “Fabrication of non-annealed anatase TiO<sub>2</sub> films on ITO conducting glasses for dye-sensitized solar cells”, 2012 International Joint Symposium between HU & CNU on Advanced Material Science & Technology, 29-30 December, Hokkaido University, Sapporo (2012)

K. Kure, Y. Konno, E. Tsuji, Y. Aoki, H. Habazaki, “Formation of Self-organized Nanoporous Anodic Films on Stainless Steel”, 5th Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st Century, 20-22 December, The University of Ryukyus, Naha (2012)

## LABORATORY OF HIGH TEMPERATURE MATERIALS

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Research work at “Laboratory of high temperature materials” directs toward 1) high-temperature corrosion of  $\text{SiO}_2$ -forming materials alloys, 2) high-temperature corrosion of stainless steels in simulated coal-firing environments, 3) oxidation of Fe-Si steels in  $\text{N}_2$ - $\text{H}_2$  atmospheres, 4) high temperature oxidation of various metal disilicides, 5) sintering of nano WC-X, and 6) hydrogen production using a  $\text{H}_2\text{O}$ -NaOH-stainless steel system.

Current topics on research are as follows:

#### (1) High-temperature corrosion of $\text{SiO}_2$ -forming alloys

High-temperature corrosion tests of  $\text{SiO}_2$ -forming alloys such as Cr-Si-Ni and CoNiCrAlY-Si alloys in molten  $\text{Na}_2\text{SO}_4$  and NaCl salts and gaseous  $\text{O}_2$ - $\text{Na}_2\text{SO}_4$ -NaCl atmospheres are being carried out. The  $\text{SiO}_2$  formers showed excellent corrosion resistance in the both atmospheres. The result demonstrates that the  $\text{SiO}_2$ -forming materials completely prevent the formation of sulfide and chloride at the scale/substrate interface and the internal sulfidation and chlorination in the substrate.

(2) High-temperature corrosion of stainless steels in simulated coal-firing environments

In order to clarify the effects of Cr content, temperature, and CO<sub>2</sub> concentration on local attack (internal sulfidation and carburization), high temperature corrosion tests of some stainless steels were carried out in simulated coal-firing environments at 600 and 700 C. The results are as follows; (1) local-internal attack beneath substrate by oxidants occurs in both of low and high CO<sub>2</sub> atmospheres, (2) the local attack is somewhat severe in the low CO<sub>2</sub> atmosphere and at the low temperature, (3) the structure of the local-attacked area is outer scale(Fe oxide)/(Cr,Fe) oxide/(Cr oxide+Cr sulfide+Si oxide)/substrate, (4) increase of Cr content in steel leads to suppression of local attack, and (6) though carburization does not probably occur even in the high CO<sub>2</sub> atmosphere, formation of carbides, probably Cr carbide, was observed in the local-attacked area.

(3) Annealing of high Si steels in N<sub>2</sub>-H<sub>2</sub> atmosphere

Annealing of Fe-(0.1-1 mass%)Si steels is being carried out in N<sub>2</sub>-H<sub>2</sub> (dew point: -65 C). Based on the results, the relationship between change of surface morphology of the steels and Si content is being studied. With increasing Si content and annealing temperature, faceted iron grains were remarkably formed on the steel surface. This is caused by the formation of internal Si oxide during cooling.

(4) High temperature oxidation of NbSi<sub>2</sub>-X(B, Ge, Al)

To improve oxidation resistance of NbSi<sub>2</sub>, a third element such as B, Ge, and Al was added into NbSi<sub>2</sub> and the influences of additives on the oxidation resistance were investigated. Ge and Al additions didn't lead to the formation of additional phases. Oxidation resistance of NbSi<sub>2</sub> was remarkably improved by B, Ge, and Al additions more than 3mass%. This is due to the formation of a low viscosity silica layer in B and Ge added NbSi<sub>2</sub> and the formation of a Al-rich oxide layer in Al added NbSi<sub>2</sub>.

(5) Sintering of nano WC powders

Nano sized tungsten carbide (n-WC) compacts with and without grain growth inhibitors were synthesized by Spark Plasma Sintering (SPS) with different heating rates. The microstructure and mechanical properties of the various samples were compared. Grain growth inhibition effects increased in the order Nb>Re>Ta>Ti and with increasing heating rate. Addition of Si and B increases grain growth, but suppresses the formation of the brittle semi carbide (W<sub>2</sub>C) phase. Using the WC-X



phase diagram and the sintering rate curves, we try to generalize the effect of various grain growth inhibitors on the sintering of n-WC.

#### (6) Development of new hydrogen production method

As a new method for the production of hydrogen, the NaOH/H<sub>2</sub>O/stainless steel system was proposed. It was actually proved that the high efficient production of high purity hydrogen could be achieved. At present, the experiments on interfacial reaction between NaOH and SUS 304 stainless steel are being done for clarifying the mechanism of hydrogen production. In the interfacial reaction, mainly iron-oxides layer consisting of FeO and Fe<sub>3</sub>O<sub>4</sub> without Cr<sub>2</sub>O<sub>3</sub> was formed.

#### Other activities

In March, Prof. Kurokawa and Mr. Kimura attended The Fifth Inter'l Workshop on Plasma Application and Hybrid Functionally Materials in Taipei, Taiwan, and presented a paper entitled "Improvement of oxidation resistance of Nb-Si intermetallics by addition of Ge". In May, Prof. Kurokawa and Mr. Sudiro attended The 8<sup>th</sup> Inter'l Symp. on High-Temperature Corrosion and Protection of Materials in Les Embiez, France, and presented a paper entitled "A Comparative Study of High Temperature Corrosion of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Forming Alloys in a Na<sub>2</sub>SO<sub>4</sub>-NaCl Atmosphere". In June, Prof. Kurokawa organized the forum on coal-firing power plants in Hokkaido Univ. In July, Mr. A. Zaki M. Zainal attended The Inter'l Symposium on ICAMME'2012 in Kuala Lumpur, Malaysia, and presented a paper entitled "The Effects of Mo addition on the structure of scales formed in high Si steel at 1150 C".

## Facilities and Capabilities

Spark Plasma Sintering Equipment

Ultra-High Vacuum Furnace with Mass Spectrometer

Oxidation Test Equipment with Thermobalance and Ultra-High Temperature Furnace

Micro-Thermobalance

Acoustic Emission system

Differential Scanning calorimeter

Scanning Electron Microscopy

Micro Vickers Hardness Tester

## Optical Microscope with High-Temperature Furnace

**Presentations**

Reaction layer and crack propagation in the Ni added Sn-Cu-Bi alloy/Cu interface; T. Yokota, K. Kurokawa, and J. Tanaka: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan. 2012.

High-Temperature Corrosion behavior of STBA21 and CoNiCrAlY-Si Alloys in the atmosphere containing Na<sub>2</sub>SO<sub>4</sub> and NaCl; T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: *ibid.*

Analysis of the initial stage sintering mechanism of spark plasma sintered nano WC; A. K. Nanda Kumar, M. Watabe and K. Kurokawa: *ibid.*

Improvement of oxidation resistance of Nb-Si intermetallics by addition of Ge; K. Kimura and K. Kurokawa: The Fifth Inter'l Workshop on Plasma Application and Hybrid Functionally Materials: Taipei, Taiwan, Mar., 2012.

Improvement of oxidation resistance of Nb silicides by Ge-addition; K. Kimura and K. Kurokawa: The 123<sup>rd</sup> Committee on Heat-Resisting Materials and Alloys JSPS: Tokyo, 2012.

Effect of Mo addition on spalling of oxide scale formed on Fe-18Cr; K. Ohtani, The 150<sup>th</sup> Annual Meeting of Jpn. Inst. Metals, Yokohama, Mar. 2012.

High-temperature corrosion of CrSi<sub>2</sub>-CoNiCrAlY alloys in an air-(Na<sub>2</sub>SO<sub>4</sub>+25.7mass%NaCl) gas atmosphere; T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: *ibid.*

Effect of Ni addition on reaction of Cu substrate with Sn-Cu-Bi solder; T. Yokota, K. Kurokawa, and J. Tanaka: Mate 2012, Tokyo, Mar., 2012.

Effect of Ni content on growth of the reaction layer formed in the Sn-Cu-Bi/Cu substrate interface during bonding; T. Yokota, K. Kurokawa, and J. Tanaka: JIEP,

Yokohama, Mar., 2012.

Mechanism and thermodynamics of formation of silica scale; K. Kurokawa: JIM Seminar, Tokyo, Mar., 2012.

Application of metal disilicides as high-temperature corrosion resistant materials; K. Kurokawa: Hokkaido Univ.-Shin-Nittetsu Joint Seminar, Sapporo, Mar., 2012.

A comparative study of high temperature corrosion of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  forming alloys in a  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  atmosphere; T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: Les Embiez, France, May, 2012.

Metal silicides possessing outstanding high-temperature corrosion and wear resistance; Coal-Firing Power Plant Seminar: K. Kurokawa: Sapporo, June, 2012.

The effects of Mo addition on the structure of scales formed in high Si steel at  $1150^\circ\text{C}$ ; Ahmad Zaki Mohd Zainal and Kazuya Kurokawa: The Inter'l Symposium on ICAMME'2012, Kuala Lumpur, July, 2012.

High-temperature corrosion of  $\text{CrSi}_2$ - $\text{CoNiCrAlY}$  alloys in mixture of  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  melts; T. Sudiro, S. Kyo, O. Ishibashi, M. Nakamori, K. Kurokawa: The 151<sup>th</sup> Annual Meeting of Jpn. Inst. Metals, Matsuyama, Sept., 2012.

Oxidation behavior of high Si steels at high temperatures in  $\text{H}_2$ - $\text{N}_2$ ; F. Sakota and K. Kurokawa, *ibid.*

A perspective on improving the fire-side corrosion resistance of boiler materials in the severe atmosphere containing  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ ; T. Sudiro, S. Kyo, O. Ishibashi, M. Nakamori, K. Kurokawa; The 59<sup>th</sup> Fall Meeting of JSCE: Asahikawa, Sept., 2012.

Application of high corrosion and wear resistant alloys as coatings to boiler tube in coal-firing power plant; S. Kyo, M. Nakamori, O. Ishibashi, and K. Kurokawa: *ibid.*

Effects of addition of third element on structure of spark plasma sintered body; A. K. Nanda Kumar, M. Watabe and K. Kurokawa: Sendai, Dec., 2012.

## **BIOMEDICAL, DENTAL MATERIALS AND ENGINEERING LABORATORY**

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The research activities cover (1)the development, evaluation and application of dental and biomedical materials, (2)the development of methods and equipments for fabrication of materials and prostheses and (3)the measurement of properties. These are concerned with mechanical, thermal properties, corrosion, surface treatment, biocompatibility, bioreactivity, estheticity and various methods of imaging and microanalyses. Many researches are related to dental, biological and engineering fields and performed in collaboration with clinical departments including Removable Prosthetic Dentistry (Prof. Atsuro Yokoyama), Orthodontics (Prof. Junnichi Iida), Operative Dentistry (Prof. Hidehiko Sano), Oral and Maxillofacial Surgery (Prof. Yasunori Totsuka), Crown and Bridge Prosthodontics (Prof. Noboru Ohata).

Current topics on research are as follows;

(1) Biocompatibility and biomedical application of carbon nanotubes(CNT) and other fine particles

Biocompatibility and cytotoxicity of carbon nanotubes(CNT), carbon nanofibers(CNF), fullerene and other nano materials were investigated. Various

type of CNT including single and multi-wall CNTs(SWCNT, MWCNT) and CNF were used with the aim of the biomedical application and the pretreatment method of purification, solubilization, dispersion, surface modification were developed. Biochemical cell functional test of cell survival rate, LDH activity, emission of oxygen radicals and cytokines IL-1 $\beta$ , IL-8, TNF- $\alpha$ , M-CSF and implantation test in soft tissue was done and bioreaction was evaluated. With the decrease of particle size the cytotoxicity originated from the physical size effect was pronounced especially below 10 $\mu$ m. Many interesting properties advantageous to biomedical application such as affinity for adhesion of cells, proteins, saccharides; precipitation of apatite in artificial salivary fluid and strong binding of pseudopodium grown into the agglomeration of CNTs as scaffold, Applications of the nanotubes as delivery system of DNA, protein, saccharic tips and the sintered bulk as implant materials are also developed.

## (2) Development of functionally graded dental implant

The dental implant with the structure of functionally graded materials (FGM) has been fabricated to satisfy different properties. The typical example is such that the composition changes from the biocompatible metal, Ti, at one end, increasing the content of ceramics, hydroxyapatite (HAP), principal component of bone and teeth, toward 100% HAP at the other end. This can control the functions of mechanical properties and biocompatibility, optimize them, depending on the necessity of each part of implant, without the abrupt change by the formation of discrete boundary. The effect of FGM structure Ti/HAP, Ti/Co on tissue response is investigated by the animal implantation test into rats and rabbits. The tissue reaction and new bone formation around the implant to the gradient composition is evaluated by both the conventional method using an optical microscope with stained specimens and by elemental mapping and other imaging methods using electron microprobe analysis(EPMA) and X-ray scanning analytical microscope(XSAM) with unstained specimens.

## (3) Modifications of carbon nanotubes for biological applications

For biomedical applications of carbon nanotubes (CNTs), new modification methods to give bioactivity or biocompatibility are needed for achievement of various required designs. Modification and immobilization of various functional molecules on CNTs by covalent and non-covalent methods were investigated. Multi-walled carbon nanotubes (MWNTs) coated with a carbohydrate-carrying polymer can be easily prepared by a non-covalent and via hydrophobic interactions. The carbohydrate coated MWNT was found to acquire a

selective binding affinity to the corresponding lectin without a nonspecific interaction. On the other hand, a bare MWNT interacted nonspecifically with lectins. These results showed that a MWNT coated with a carbohydrate-carrying polymer has the biological recognition signals. Secondly, we developed a biomimetic coating method to produce the architecture of crystalline apatite at nano-scale levels on the surface of MWNTs. After immersion of MWNTs in revised simulated body fluid (r-SBF), the crystallites at nano level were grown radially originating from a common center in the middle of a single MWNT and perpendicularly to the longitudinal direction of MWNT. MWNTs with the defined surface morphology of nano apatite crystallites could be useful as biomaterials for scaffolds and for the biomedical applications.

#### (4) Development of FRP esthetic orthodontic wire

To realize the esthetic, transparent orthodontic wire the FRP wires of the diameter 0.5mm with the multiple fiber structure has been fabricated by either drawing of fiber-polymer complex at 250C or photopolymerization method. Biocompatible  $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$  (CPSA) glass fibers of 8-20 $\mu\text{m}$  in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bis-GMA. The improvement has been done to obtain the adequate flexural strength and higher torque. FRP wire shows the sufficient flexural strength and a very good elastic recovery. The dependence of Young's modulus and flexural stress on fiber fraction obeys very well the rule of mixture. This FRP wire can cover the range of the strength corresponding to the conventional metal orthodontic wires from Ni-Ti used in the initial stage of orthodontic treatments to Co-Cr used in the last stage by changing the volume ratio of glass fibers with the same external diameter. FRP wire can satisfy both mechanical properties and estheticity, which is not possible for the conventional metal wire.

#### (5) Cytotoxicity due to ions and fine particles of Ti and other metals in vivo and in vitro:

The removal of Ti plates for fixing jaw bone in 6 months after operation often reveals the slightly dark colored tissue in the circumferential soft tissue. The observation and analysis by optical microscopy, electron microscopy and XSAM revealed that the colored tissue contains the abraded fine particles of Ti, probably produced during plate fixation in operation.

The animal experiments to implant various sizes of Ti particles of 1-100 $\mu\text{m}$  and macroscopic cylindrical Ti implant in  $\mu\text{m}$  order for 3 days to 8 months showed that the macroscopic size of Ti was encircled with fibrous connective tissue layer

from early stage and there was no inflammation. As the size of particle becomes smaller, many phagocytic cells appear with fibrous connective tissue layer inside the particle inserted region and tissue showed inflammation. It takes more time to encircle the particle-contained tissue region and heal inflammation. For 1-3 $\mu$ m the inserted region is never encircled with fibrous connective tissue layer and inflammation continues.

The in vitro cell functional tests on cell survival rate, LDH(Lactate Hydrogenase CII) protein released at the breakdown of cell membrane and superoxidized anion(O<sup>2-</sup>) using human neutrophils showed that Ni solution has the cell disruption effect. The deformed and disrupted morphology of neutrophils was confirmed by SEM observation. Whilst Ti and V solution showed the increase of superoxide anion and negligible change in the others, which suggests the cell stimulation effect. SEM observation confirmed that neutrophils are inflated with more complicated polyacicular morphology. One of the marking cytokines released at phagocytization, TNF- $\alpha$ , was not detected in any solution of Ni, V, Ti, the simulated body fluid(Hank's solution) mixed with 10 $\mu$ m particles of Ti and with submicron size Ni particles. TNF- $\alpha$  was found only in the 1-3 $\mu$ m Ti particle mixed Hank's solution, which suggests that particles were phagocytized. SEM observation and EDS elemental analysis confirmed the phagocytosis of Ti particles by neutrophils.

The difference of cell reaction to 1-3 $\mu$ m and 10 $\mu$ m Ti particles suggests that the particles(1-3 $\mu$ m) smaller than cell size(about 5 $\mu$ m in neutrophils) induces cytotoxicity as a result of phagocytosis, while for particles larger than cell size(10 $\mu$ m) phagocytosis is not possible, resulting in the less clear cytotoxicity effect.

The study shows the cytotoxicity originating from physical size effect of particles other than biochemical toxicity effect, which is significant for the cases where the fine particles are produced during abrasion by long term usage of moving parts in the artificial bone joint.

(6) In situ observation of etching process of human teeth in acid agent by atomic force microscopy

Composite resin with fillers of ceramic powders in polymer matrix has estheticity similar to natural teeth color and is widely used for treatments of caries in incisal teeth. Physical-mechanical anchoring effect plays an important part in binding force between teeth and composite resin. The pretreatment to make etching of teeth is generally done using acid agents for enhancement of binding. SEM is usually used for the evaluation of etching effect. It can observe, however,

only the result after a certain etching time. To observe the sequence of etching process it is necessary to prepare the series of specimens treated with different etching time. Atomic force microscope is applied for the in-situ observation of etching process of human enamel and dentin in acid agents. The chronological change of surface morphology can be successively observed and quantitative analysis is done for different etching conditions.

(7) Fabrication of composite resin prostheses by laser lithography:

Laser lithography, one of the CAD/CAM systems to fabricate the polymer models by piling up the thin slices, which are photo-polymerized by scanning laser beam originally on the shallow depth of liquid epoxy monomer, was applied for the fabrication of dental prostheses of photo-curing composite resin composed of silica fillers in the matrix of high strength UDMA resin. The full dental crown could be fabricated using the shape data pre-designed by computer with high accuracy due to the smaller polymerization shrinkage than by conventional methods. Then the functionally graded dental core and post with gradually changing filler content from 70 to 0% from the head of core abutment toward the apex of post was successfully fabricated. The stress concentration at the pulp root inserted with the conventional dental post has often caused the fracture in the surrounding dentin by impact force on the tooth crown. The stress relaxation effect by application of the functionally graded dental post was confirmed by simulation using the photoelastic method and finite element method(FEM).

(8) Radiation effects on polymer resin :

Radiation effects by  $C^+$  ion,  $\gamma$ -ray from  $Co^{60}$  and electrons on one of the main matrix polymer UDMA(urethane dimethacrylate) for dental composite resin were investigated with various mechanical tests and spectroscopies.  $C^+$  ion radiation induced the large change in the structure sensitive properties of mechanical properties, Vickers hardness, flexural strength, abrasion resistance and little change in the non-structure sensitive properties of spectroscopies, FT-IR, Raman scattering, Fluorescence, NMR and thermal expansion coefficient. The results suggest that the mechanism of radiation effect is mostly due to the physical structure change such as lattice defects of vacancies, interstitials, depleted zone rather than the chemical effect of cross-linking by further progress of polymerization of residual monomers.

(9) Evaluation of biocompatibility of refractory metals and their application

Refractory metals of IVA group(Ti, Zr, Hf), VA group(V, Nb, Ta) and



VIIA group(Re) are investigated in their biocompatibility and other bioreactivities. Animal implantation tests show that the fraction of direct contact of newly formed bone to implant material without intervening of fibrous connective tissue at the interface and the amount of new bone vary depending on materials. The composites of these refractory metals are also made and the comparison and the composite effect is investigated.

(10) Surface treatment of dental and biomedical materials with sol-gel method

Biocompatibility and adhesivity to tissue is important for dental materials. Various dental metals were coated by amorphous silica gels with sol-gel method. In some cases, biocompatibility were improved.

(11) Tissues and dental materials observation by XSAM

The scanning X-ray analytical microscope (XSAM) was applied for the analysis of the soft tissue of rat in which various metals including Fe, Cu, SUS, V, Co, Ni were implanted. The dissolution of implanted metals and inflammation of tissues were observed by elemental mapping image obtained by XSAM.

(12) Bonding property and cytotoxicity of dental zirconia ceramics (YPSZ)

Ytria partially stabilized zirconia (YPSZ) ceramic is suitable for dental and medical use because of its high fracture toughness and chemical durability. The bonding properties of dental zirconia with various luting cements and surface treatments are investigating. The cytotoxicity dental zirconia ceramics compared to other dental ceramics was also evaluated.

(13) Abrasion-resistant implant made of refractory metal nitrides and carbides

Surface-nitrided titanium(Ti(-N)) showed high corrosion resistance and nearly equivalent biocompatibility with Ti in soft and hard tissue in animal implantation test. Surface durability was evaluated by three static and dynamic mechanical tests; Vickers hardness test, Martens scratch test and for more practical viewpoint newly developed abrasion test using ultrasonic dental scaler which is used to remove calculus on teeth in dental clinics. Vickers hardness of Ti(-N) was 1300, ten times larger than Ti. Martens scratch test showed that the bonding of nitrided layer with 2 $\mu$ m thickness is coherent to matrix Ti and enough strong. Abraded volume by ultrasonic scaler was increased with the load in Ti, while no trace was formed in Ti(-N), instead stainless tip of scaler was abraded. The test showed that abrasion would be negligibly small under the practical conditions of the load 50g in clinics. Ti(-N) with biocompatibility and surface abrasion resistance

would be suitable as abrasion-resistant implant materials for the application to the artificial joint of implant and abutment part of dental implant.

(14) Development of visible-light responsible photocatalysis and its application

The current photocatalysis of anatase  $\text{TiO}_2$  mostly works only by ultraviolet light. To make applicable for medical use it is necessary to develop the visible-light reactive photocatalysis. Visible light sensitization was obtained by surface modification with cations of Au, Ag, Cu, Pt, Pd. Depigmentation with visible light around 470nm which is used for photopolymerization of composite resin restoration in dental clinics could be done with the Ag activated  $\text{TiO}_2$  in contrast to very little effect in an untreated  $\text{TiO}_2$ . Antibacterial effect was also confirmed to streptococcus mutans, one of the most popular bacteria for caries. The application to bleaching of pigmented teeth was developed.

(15) Development of discrimination method of resin-restored teeth

In the health checkup in school mass of patients must be checked in the limited time. Due to the recent development of estheticity of composite resin it is now very difficult to recognize the resin-restored teeth and discern resin part from natural teeth. Total reflection spectroscopy and fluorescence spectroscopy were measured and images were taken with reflected light and fluorescence light using the filters to select the appropriate wave length. In the long wave length region for more than 600nm the reflectivity of teeth is higher than that of composite resin. The image formed with filtered light, however, did not show the contrast enough to discern the resin part from tooth. For less than 400nm both teeth and resin showed the fluorescence emission with high and comparable intensity. For the light of 430-450nm teeth emitted higher fluorescence and the relative difference is larger. The images formed with fluorescence light for more than 500nm emitted by 430-450nm light excitation showed the easily recognized contrast to discriminate resin from tooth.

(16) Microparticles of biodegradable polymers with controlled structure for drug delivery system

Single and double emulsification solvent evaporation method is extensively used for more than two decades for the encapsulation of various substances from simple pharmaceutical products to proteins and DNA.

Particle formation mechanism is crucial for size distribution, and morphology, which in turn determine the delivery system behavior during encapsulation and release.

In order to identify and quantify the main influence parameters that determine the microparticle performance as drug delivery system, the mechanism of particle formation of biodegradable polyesters: poly(DL-lactide co glycolide) and poly(L-Lactide), was investigated in their single and double emulsion formulation.

In situ optical microscopic investigations showed that the microparticles are formed by accelerated solvent elimination due to the combined effects of high solvent volatility and polymer precipitation. The fast shrinkage that accompanies the solvent elimination has important influence on the particle morphology. Scanning electron microscopy and laser diffractometry evidenced the presence of a thin nanoparticulate layer on the microparticles surface. This layer is formed during the solvent elimination by the shrinkage-induced fragmentation of the precipitating polymer. It is reasonable to believe that the encapsulated substance will accumulate in this layer contributing to the initial burst release.

The inner aqueous phase in the double emulsion formulations has important influence on the mechanism of particle formation. In this case microparticles with different structures are generated. The proportions of microparticles with different structure are determined mainly by the stirring rate and the polymer concentration.

During solvent elimination the droplets of inner aqueous phase coalesce under the precipitating polymer pressure. Due to the incompressibility of the inner aqueous phase, the polymer wall often breaks resulting in holes through which the inner aqueous phase is partly expelled. Furthermore, after particle hardening the holes will contribute to the encapsulated substances leakage through partitioning with the external aqueous phase, and to the initial burst release.

Other activities:

Dr. Xiao Chen of Huazhong University of Science and Technology, China joined to our laboratory on March 2012 as the postdoctoral researcher of the Japan Society for Promotion of Science (JSPS) for “Application of unique cell membrane permeability of carbon nanotubes for anti-cancer therapy”.

The international collaborations are continued with Institute of Dental Materials Science, Umea University, SWEDEN (Emerita Prof. Maud BERGMAN) on application of Ti, ZrO<sub>2</sub>, amalgum for dentistry, and research on side effects, with Department of Dental Materials, Chonbuk National University, KOREA (Prof.Tae-Sung BAE) on evaluation of mechanical properties of laser-welded Ti, dental porcelain, with Institute for Materials Science, Dresden Institute of Technology, GERMANY (Prof.W.POMPE) on the biocompatibility evaluation and application of collagen-hydroxyapatite composites and with Biomaterials

Laboratory, Department of Materials Science and Engineering, Tsinghua University, CHINA (Prof.FZ CUI) on the development and biomedical application of nanobiomaterials, University Polytechnica Bucharest, Bucharest, Romania (Dr. ROSCA Iosif Daniel) on the development of polymer biomaterials.

## Facilities and Capabilities

XSAM: HORIBA XGT-2000V, Scanning X-ray analytical microscope for elemental mapping analysis

XRD: Rigaku Multiflwx, X-ray diffractometer (3kVA)

AFM : TopoMetrix TMX2000 Explorer, AFM for dry and wet specimens

NSOM : TopoMetrix Aurora, Near field Scanning Optical Microscope

Laser Raman Spectrometer : Dilor Labram, Laser Raman Spectrometer with mapping analysis

ICP : HITACHI P-4010, ICP emission spectrometer for analysis of elements in aquaous solution

FT/IR : Jasco FT/IR-300E, FT/IR spectrometer with microscopic IR measurement

Particle Size Analyzer : Shimadzu SALD-7000, Particle size distribution analysis with laser scattering

Surface Area Analyzer : Shumadzu, Surface area analysis with gas absorption/desorption

Universal Testing Machine : INSTRON MODEL 4204, Testing for mechanical properties of materials

Laser Welder : ATJ TLL7000, Nd-YAG pulse laser welder with computer controlled x-y stage

Cold Isostatic Press : Hiikari Koatsu Kiki (10000atm type and 20000atm type)  
:Kobelco, Large volume isostatic press (4000atm)

Vickers Hardness Tester: Shimadzu

Acoustic Emission : Physical Acoustic Corporation

Thermal Gravimetry and Differential Thermal Analysis(TG/DTA) : Rigaku Denki

Diamond Cutter : Buehler and Struers diamond cutter

## Presentations

Cell Culture on Carbon Nanotube Thin Films Murine Macrophage RAW264.7 Cells Response for the Carbon Nanotubes Immobilized on

Substrate, Tsukasa AKASAKA, Shigeaki ABE, Fumio WATARI, the 24th Symposium and Annual Meeting of International Society for Ceramics in Medicine, Fukuoka, Oct.22-24, 2012

Cell Culture with Carbon Nanotube Films and Cell Manipulation, Tsukasa AKASAKA, Shigeaki ABE, Fumio WATARI, the 59th General Session of the Japanese Society for Dental Materials and Devices, Tokushima, Apr.14-15, 2012

Anti-bacterial Activity of Chitosan Film with Nano-structure, Tsukasa AKASAKA, Shigeaki ABE, Fumio WATARI, the 60th General Session of the Japanese Society for Dental Materials and Devices, Fukuoka, Oct.13-14, 2012

Analysis of Surface Properties of Dental Zirconia; N Tarumi, F Watari, the 60th General Session of the Japanese Society for Dental Materials and Devices, Fukuoka, Oct.13-14, 2012

An Application of Fluorescent Matter to Bonding Materials; Y.HAMBA, S.YAMAGATA, T.AKASAKA, M.UO, J.IIDA, F.WATARI, 59th The Journal of the Japanese Society for Dental Materials and Devices, Tokushima, Apr.14-15, 2012

Characteristic Evaluation of Dental Bonding Materials with Fluorescence Properties; Y.HAMBA, S.YAMAGATA, T.AKASAKA, M.UO, J.IIDA, F.WATARI, 60th The Journal of the Japanese Society for Dental Materials and Devices, Fukuoka, Oct.13-14, 2012

SEM observation of carbon nano materials using ionic liquids; S.Abe, A.Hyono, T.Yonezawa, F.Watari, ISPlasma2012, Kasugai, March 2012

Bidistribution and biocompatibility of nano-sized materials: An in vivo and in vitro study; S Abe, N.Iwadera, A.Sasaki, S.Itoh, T.Narushima, Y.Uchida, T.Akasaka, M.Uo, Y.Yawaka, T.Yonezawa, F.Watari, 9th World Biomaterial Congress 2012, Chengdu, China, June 2012

Controlled calcification using biomimetic enzymes with zinc coordinated compound: A carbonate ion induced calcification; S.Abe, M.Yohda, Y.Fujii, E.Yamatoya, T.Ishida, T.Akasaka, F.Watari, M.Uo, D.Hayashi, T.Takada, 19th International SPACC Symposium, Sapporo, Aug. 3, 2012

Photophysical properties of self-assembled cyanine-dye aggregates formation assisted by cyclodextrin inclusion complexation; S.Abe, T.Kiba, T.Hirota, N.Miyakawa, F.Watari, A.Murayama, S.Sato, KJF2012, Sendai, Aug. 31, 2012

Biocompatibility and biodistribution of several nano-sized ceramics particles, S.Abe, Y.Hamba, N.Iwadera, T.Akasaka, S.Yamagata, Y.Yawaka, J.Iida, M.Uo, T.Yonezawa, F.Watari, 24th International Symposium on Ceramics in Medicine, Fukuoka, Oct. 22, 2012

Photophysical properties of europium doped ceramics nanoparticles in bio/medical polymer matrix; S.Abe, Y.Hamba, S.Yamagata, M.Uo, J.Iida, T.Kiba, A.Murayama, F.Watari, MNC2012, Kobe, Nov. 1, 2012

SEM observation of nano structured materials using Room Temperature Ionic Liquids, S.Abe, F.Watari, A.Hyono, T.Yonezawa, ICNME2012 (Awaji), Dec. 13, 2012

## **ECO-PROCESSING LABORATORY**

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### **Foreign Researchers**

Xiang Ning MENG

### **Students**

M. Baba, H. Nishiyama, R. Enmei, I. Ueda, T. Fujisaka, H.T. Sui,  
S. Egawa, M. Yoshida, A. Nakagawa, A. Sado, T. Yamamoto, T. Uchiyama  
K. O. Ito, O. Nishinaga, R. Ishida, T. Wakamatsu

Prof. Ryosuke O. Suzuki merged as the professor of the laboratory of Eco-processing from Kyoto University on March 2006. He began to study the non-ferrous metallurgy based on the molten salt electrolysis. The research activities of his group are directed to design the economical and environment-friendly processes for materials at high temperatures. The extraction metallurgy of the refractory metals such as niobium and tantalum, and of valve metals such as titanium, vanadium and zirconium, contains many topics when the electrolysis of CaO in the molten CaCl<sub>2</sub> is applied. The electrolysis of CO<sub>2</sub> gas is one of the extreme case in the field for oxide decomposition. The thermoelectric power generation is designed from the view of material design and heat exchange between two thermal fluids.

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 electrochemical techniques such as anodizing, electrochemical etching, and electrodeposition. 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.

Current topics on corrosion research are in the following:

(1) Molten salt electrolysis of  $\text{CaCl}_2$

Reduction of the oxides of titanium, niobium and tantalum are studied when the CaO dissolved in the molten  $\text{CaCl}_2$  is electrochemically decomposed to form metallic calcium. A low oxygen potential can form the metallic powders at the cathode. The reduced metallic powder is prepared directly from the oxides as well as CaO. The homogeneous metallic alloy powder can be synthesized from the oxide mixture using the same method. The mechanism of this proposal is examined from the electrochemistry and thermodynamics.  $\text{CO}_2$  gas reduction gets the current interest in the morphology of precipitated carbon particles.

(2) Micro- and Nano-structure fabrication by anodizing

Porous type anodic oxide film of aluminum has been widely investigated and used as a nanostructure template in various nanoapplications. The porous layer consists of numerous hexagonal cells perpendicular to the aluminum substrate and each cell has several tens or hundreds of nanoscale pores at its center. We have been working on a new nanoporous anodic alumina formed by several electrochemical techniques. Our new nanoporous alumina can be used as a nanotemplate for various nanostructures in 100-, 10-, and sub-10-nm-scale manufacturing.

Other activities

(1) Thermoelectric power generation

An optimization of the thermoelectric power generation is mathematically designed to generate the maximum output. The heat exchange between the two fluids is optimized to give the largest temperature difference along the large thermoelectric panels. This work may link with the energy source for electrolysis. The utilization of solar energy is challenged using cheap materials.

Prof. R.O. Suzuki was invited at 4th Asian Conference on Molten Salt Chemistry and Technology, and presented the keynote lecture on “Reduction of Niobium Oxide Using  $\text{CaCl}_2$  Melt”.



The following foreign scientist visited this laboratory : Dr. XiangNing Meng, Northeastern University, China, joined in our group as JSPS postdoctoral fellow on August 2012 for 2-years project.

## Presentations

Fabrication of anodic oxide film by phosphoric acid anodizing at over 200 V; I. Ueda, T. Kikuchi, R. O. Suzuki, and Li Ronghua : The 29<sup>th</sup> Anodizing Research Society Conference, Izu-Nagaoka, Japan, Nov., 2012.

Formation behavior of aluminum nano-dimples by anodizing in malic acid solution; T. Yamamoto, T. Kikuchi, and R. O. Suzuki : *ibid.*

Fabrication of a micro-porous titanium alloy by electroless reduction with a calcium reductant for electrolytic capacitor applications; T. Kikuchi, M. Yoshida, and R. O. Suzuki : *ibid.*

Dimensional Optimization of Thermoelectric Modules for Solar Power Generation; Takeyuki Fujisaka, R. O. Suzuki: The 38th Annual Conference of the IEEE Industrial Electronics Society, IEEE- IECON2012, 25-28 October 2012, ÉTS, Montréal, Canada.

Power Generation Using the Fluids Blown Perpendicular to the TE Panel; R.O. Suzuki, Yuto Sasaki, Takeyuki Fujisaka, and Min Chen: *ibid.*

Optimization of Design in Cascade-Type Thermoelectric Module; R.O. Suzuki, T. Fujisaka: Powder Metallurgy World Congress & Exhibition PM2012 Yokohama, 14-18 October 2012, Yokohama, Japan

Fabrication of Flexible Alumina Microlens Array by Laser Irradiation and Aluminum Anodizing: T. Kikuchi, Y. Wachi, T. Takahashi, M. Sakairi, and R. O. Suzuki; 222nd the Electrochemical Society Meeting, PRiME2012, Honolulu, Hawaii, USA, Oct., 2012.

Decomposition of CO<sub>2</sub> Gas in CaCl<sub>2</sub>-CaO and LiCl-Li<sub>2</sub>O Molten Salts; R.O. Suzuki, K. Otake, T. Uchiyama, H. Kinoshita, T. Kikuchi: *ibid.*

Thermoelectric Generation Using Water Lens Concentrating Solar Heat; R.O. Suzuki: JST-EPSRC, JST-MOST & CREST Joint Workshop on Thermoelectrics, 2-3 October, 2012, Nagoya University, Nagoya

Fabrication of titania nanotube layer by anodizing in fluoride and chloride solutions; A. Sado, T. Kikuchi, and R. O. Suzuki : The 126<sup>th</sup> Annual Meeting of Surf. Finish. Soc. Jpn., Muroran, Japan, Sep., 2012.

Fabrication of anodic porous alumina by anodizing in several dicarboxylic acid solutions; T. Yamamoto, T. Kikuchi, and R. O. Suzuki : *ibid.*

A new fabrication process of Ti-Zr alloy microparticles for electrolytic capacitor applications; T. Kikuchi, M. Yoshida, and R. O. Suzuki : *ibid.*

Apparatus and Technology to decompose CO<sub>2</sub> gas into carbon and oxygen; R.O. Suzuki, Innovation JAPAN 2012, 27-28 September 2012, Tokyo International Forum, Tokyo

Reduction of Niobium Oxide Using CaCl<sub>2</sub> Melt, R.O. Suzuki. 4th Asian Conference on Molten Salt Chemistry and Technology, (also 44th Symposium on Molten Salt Chemistry, Japan), 23-27 September, 2012, Matsushima, Miyagi

Electrochemical Reduction of Oxidized Neodymium Scrap in CaCl<sub>2</sub>-CaO melt; Ryunosuke Enmei, Hiromichi Nishiyama, Tatsuya Kikuchi, R.O. Suzuki: *ibid.*

CO<sub>2</sub> decomposition and Formation of CNT by molten salt electrolysis; Takuya Uchiyama, Norihito Sakaguchi, Koya Otake, Tatsuya Kikuchi, R.O. Suzuki: *ibid.*

CO<sub>2</sub> decomposition using Li<sub>2</sub>CO<sub>3</sub> melt and ZrO<sub>2</sub> solid electrolyte; T. Uchiyama, N. Sakaguchi, K. Otake, T. Kikuchi, R.O. Suzuki: 164th Annual Meeting of Iron and Steel Institute of Metals, Fall session, 17-19 September 2012, Ehime University, Matsuyama, Ehime

Fabrication of a nano-dimple array by self-ordering anodizing; I Ueda, T. Kikuchi, R. O. Suzuki, Li Ronghua : *ibid.*

Fabrication of electrode materials for electrolytic capacitor by electroless reduction of TiO<sub>2</sub>/ZrO<sub>2</sub> mixture with a calcium reductant; M. Yoshida, T. Kikuchi, and R. O.

Suzuki : *ibid.*

A novel recycling process of neodymium magnet by electroless reduction with a calcium reductant; H. Nishiyama, T. Kikuchi, and R. O. Suzuki : *ibid.*

Simulation using Water Lens for Thermoelectric Generation; Hongtao Sui, T. Fujisaka, R.O. Suzuki: 9th Annual Meeting of the Thermoelectrics Society of Japan 2012 (TSJ2012), 27-28 September 2012, Tokyo Institute of Technology, Tokyo

Optimization of Multi-stage Thermoelectric Modules for Power Generation by Numerical Analysis; T. Fujisaka, Hongtao Sui, R.O. Suzuki: *ibid.*

Carbon precipitation from CO<sub>2</sub> gas using the molten salt electrolysis of Li<sub>2</sub>CO<sub>3</sub>; T. Uchiyama, N. Sakaguchi, K. Otake, T. Kikuchi and R.O. Suzuki: The Summer Sessions of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., 24 July 2012, Hokkaido University, Sapporo Hokkaido

Fabrication of titania nanotube layer by anodizing in chloride containing solution; A. Sado, T. Kikuchi, and R. O. Suzuki : *ibid.*

Fabrication of anodic porous alumina by anodizing in dicarboxylic acids; T. Yamamoto, T. Kikuchi, and R. O. Suzuki : *ibid.*

Fabrication of Ti-Zr microparticles by calciothermic reaction; M. Yoshida, T. Kikuchi, and R. O. Suzuki : *ibid.*

Self-ordering behavior of anodic porous alumina; I Ueda, T. Kikuchi, R. O. Suzuki, Li Ronghua : *ibid.*

Calciothermic reaction of neodymium oxide in molten salt at high temperature; H. Nishiyama, T. Kikuchi, and R. O. Suzuki : *ibid.*

Fast Reduction Starting from CaTiO<sub>3</sub>; R.O. Suzuki, N.Kobayashi, K. Kobayashi, K. Egawa and T. Kikuchi: 3rd International Round Table on Titanium Production in Molten Salts, 17-19th July 2012, Fitzwilliam College, Cambridge, UK

Thermoelectric Generation Using Water Lens; R.O. Suzuki, Atsushi Nakagawa,

Hongtao Sui and Takeyuki Fujisaka: 31st International Conference on Thermoelectrics (ICT2012), 9-12 July 2012, Aalborg, Denmark

Using water lens for thermoelectric generation; Hongtao Sui, Takeyuki Fujisaka and R.O. Suzuki: *ibid.*

Design and Numerical Evaluation of Cascade-type Thermoelectric Modules; Takeyuki Fujisaka, Hongtao Sui, R.O. Suzuki: *ibid.*

CO<sub>2</sub> decomposition using molten salts and zirconia; R.O. Suzuki, Y. Kashiwaya, H. Sakai, K. Otake, T. Kikuchi: 4th Meeting of ISIJ Research Group of Carbon Circulation Steel Refining, 7th June 2012, Hokkaido University, Sapporo, Hokkaido

Fabrication of a microlens array made of anodic alumina by mechanical machining and electrochemical techniques; T. Kikuchi, T. Takahashi, and R. O. Suzuki : The 122<sup>nd</sup> Annual Meeting of the Japan Institute of Light Metals, Fukuoka, Japan, May, 2012.

## 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> gas with RF heating and they are detected by the infrared absorption method. 6mass%-0.6 mass ppm.

CO/CO<sub>2</sub> Gas Analyzer IR-400: 4 sets. Yokogawa. In the range of 0.1 vol% and 10 vol%.

NO/SO<sub>2</sub> Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 2 vol%.

Constant voltage generators: Takasago Electric. 4 sets. Max.50V and 20 A.

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

Ozone gas generators: 2 sets. max 8 vol%O<sub>3</sub> gas using O<sub>2</sub> gas.

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

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

temperature.



## **AFFILIATE MEMBERS**





## AFFILIATE MEMBER

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### Students

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Our group has been investigating the subjects related to corrosion engineering, surface finishing of metals, and development of new technologies of electrochemistry. Current topics are followings:

(1) Al coating on Mg alloy from molten salt bath.

Mg alloys are attractive material because of their light weight, high strength and rich resource in nature. However, their weak corrosion resistivity limits practical application. Corrosion protective surface coating for Mg alloys have been, therefore, developed in our laboratory such as chemical conversion coating combined with electrochemical polarization and optimized zincate pretreatment for electro/electroless metal plating. Electroplating of Al on AZ91D from  $\text{AlCl}_3 : \text{NaCl} : \text{KCl}$  molten salt bath has also been therefore explored. Molten salt bath has advantages of low cost, high plating rate and low water content as impurity. Activation process, Zn under-coating process including Cu nano-particle pre-deposition and zincating and Al electrodeposition process using galvanostatic bipolar pulse polarization technique were optimized to obtain Al coating with better adhesivity and uniformity on AZ91D.

(2) Corrosion monitoring of thin Cu film in high temperature solution using resistometry.

Copper is a candidate material for metal container used for depository of radioactive nuclear wastes produced in atomic power plants. The container will be stored deep-underground to be separated from civilian areas. In the previous research corrosion rate of Cu was considerably affected by the silica contained in the environmental solution. The role of silica on corrosion behavior of Cu was therefore investigated. Silicate film was formed on Pt electrode and thickness,

morphology, composition and influence of it on electrochemical property were evaluated by using SEM, EDS, Laser Raman spectroscopy, and electrochemical impedance method. The results showed that the presence of silicate film of about 1  $\mu\text{m}$  in thickness did not affect polarization curve or impedance response of Pt electrode although the coating considerably reduced the corrosion rate of Cu immersed in 0.01M  $\text{Na}_2\text{SO}_4$  solution. These results indicated clearly that the film prevented the transportation of the species related to the corrosion reaction but not the electrochemical reaction. However, the silicate film could not suppress corrosion if  $\text{NH}_4^+$  ions existed. Mechanism of Cu corrosion under silicate film was proposed.

### (3) Development of pH sensors durable in high temperature aqueous solution.

pH is an one of the dominant factor in corrosion phenomena and thus measuring pH in the practical corroding system has been an important issue. Application of commercially available pH sensor to monitoring the local corrosion inside the pits or aqueous corrosion in high temperature water is difficult because of its limitation in size, structural weakness, low durability at operation temperature. pH sensor composed of Ir oxide powder, carbon powder, teflon powder and polyethylene powder as binder was therefore fabricated in a glass tube. Sensitivity (mV/pH) and response time, mechanical strength and durability in hot water, and degradation in long term storage were evaluated.

### (4) Application of micro-plasma to a flow system

Micro-plasma can be generated at the narrow gap in a glass tube by applying high AC or DC voltage between the electrodes placed in the liquid flowing the glass tube even in the low electric conductive medium. Mixture of various alcohol and aqueous solution containing KCl was used for flowing medium to investigate decomposition performance of organic compound by micro-plasma. Spectroscopic measurement of light emitted from micro-plasma revealed that the alcohol molecule was decomposed into fragments such as CH and C<sub>2</sub>. Decomposition efficiency was investigated as a function of high-voltage, flow rate, composition of solvent, and electric conductivity of solution. Evaluation of plasma temperature by computer simulation of optical spectra confirmed that the micro-plasma was nonequilibrium state of radicals such as  $\text{OH}\cdot$  at temperature in the order of thousands and electron at temperature higher than 10 thousand degree. Hydrophobic solvent such as cyclohexane was also evaluated by using detergent agents to form micell.

(5) Experimental and theoretical study of effect of additives on Ni electrodeposits

Structures of Ni films electrodeposited from a Watts bath containing additives of 2-buthyne-1,4-diol (BD) were investigated using SEM, SIM, XRD and traditional electrochemical methods. Preferred orientation of Ni electrodeposits was assigned to potential domains for electrodeposition. The growing axis of Ni electrodeposits seems to agree with the speculation from Pangarov's model based on the two-dimensional nuclei theory in the lower overpotential region, although the growth axes of Ni deposits do not always agree with the preferred orientation. Adsorption of BD affects the structure and morphology of electrodeposits via an inhibitory effect related to its surface coverage depending on surface orientation, growth rate and BD concentration in the plating bath. Density functional theory (DFT) calculation was also applied to evaluate quantitatively the adsorption energies of additives on model Ni clusters and their electronic states and density. Analysis of a natural electron configuration of adsorbates before and after adsorption on Ni clusters clarified that the 2s orbital rather than other orbitals such as 2p contributed mainly to the adsorption energy.

## Presentations

A. Shaaban, S. Hayashi, K. Azumi; Promotion of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation on Ni-Al alloy using Ni-Fe<sub>2</sub>O<sub>3</sub> nano-composite seeding layer, NTHH Symposium, Dec. 20th-21st (2012), Naha, Okinawa.

K. Azumi, H. H. Elsentriecy, J. Tang; Development of corrosion protective Al coatings for Mg alloys, *ibid.*

Y. Sato and K. Azumi; Corrosion inhibition by zinc corrosion products on zinc-coated steel, 222nd Meeting of ECS - The Electrochemical Society 2012 Fall Meeting of The Electrochemical Society of Japan (PRiME 2012), Oct.7-12, 2012, Honolulu, Hawaii

H. Tamai, M. Hafner, A. Hassel, H. Tachikawa, and K. Azumi; evaluation of micro plasma formed in the narrow gap in electrolyte solution, *ibid.*

H. Tamai, H. Tachikawa, K. Azumi, Martina Hafner, Achim Walter Hassel; Formation and characterization of micro-plasma, The 126th Annual Meeting of Surf. Finish. Soc. Jpn., Sep., 2012, Muroran.

Yu Fang, M. Ueda, K. Azumi; Optimization of Al plating on AZ91D from molten salt bath, *ibid*

A. Shaaban, S. Hayashi, K. Azumi, Improvement of high-temperature oxidation resistance of Ni-Al alloy using nano-composite Ni-Fe<sub>2</sub>O<sub>3</sub> seeding layer, 59th Annual meeting of Japan Society of Corrosion Engineering, 2012, Asahikawa.

S. Arikura, K. Azumi; High durable IrOx composite pH sensor, *ibid*.

Y. Sato; Time- and spatial-resolved observation of atmospheric corrosion of zinc-coated steel by using 100-muitichannel electrode method, Symposium on AGH University and Hokkaido University, AGH- University of Science and Technology, Cracow, Sept. 3rd-6th, (2012)

K. Azumi; Recent progress in corrosion protection coatings on magnesium Alloys, *ibid*.

T. Nosaka, K. Azumi; Decomposition of VOC using Cu nanoparticle modified WOx photo-catalyst, 79th Annual Meeting of Electrochemical Society of Japan, March, 2012, Hamamatsu.

Y. Sato, K. Azumi; Corrosion inhibition of Zn plated steels in atmospheric corrosion due to Zn corrosion products, *ibid*.

K. Suetake, K. Azumi; Size effect in plating process of AL micro-electrode, *ibid*.

H. Tamai, M. Hafner, A. W. Hassel, K. Azumi; Conditioning and characterization of micro-plasma formation under atmospheric pressure, Winter Joint Meeting of the Hokkaido Branch of the Chemistry Related Societies, February, 2012, Sapporo.

Y. Aoki, K. Azumi; Development of pH sensor for high temperature water, *ibid*.

K. Suetake, K. Azumi; Size effect of Al microelectrodes, *ibid*.

J. Yajima, K. Azumi, M. Watanabe, N. Taniguchi, R. Shimizu; Influence of ionic species in underground water on corrosion rate of Cu, *ibid*.

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The research activities of the laboratory are directed to the materials surface science and engineering. We are interested in the micro-electrochemistry for a better understanding of the interfacial phenomena of metal and semiconductor electrodes in relation to electrochemical devices, corrosion, passivation, and surface finishing.

Current topics on research are as follows:

#### (1) Grain-dependent Passive State of Iron Single Grains in Sulfuric Acid

Anodic polarization of pure iron surface was carried out in sulfuric acid using a micro-capillary cell. The polarization of single grains revealed that the surface morphology was strongly affected by the selective dissolution in the direction of  $\langle 001 \rangle$  during active state. The formation and dissolution of oxide film depended on crystallography of the surface. The electric charge and final current densities after 3.6 ks potentiostatic polarization at 1.0 V (SHE) became larger in the order of  $001 < 111 < 101$  grains. Electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy were suggested that the order was due to accumulation of dissolved ferrous species during active state as well as film thickness formed in passive state.

#### (2) Corrosion Behavior of Dual-Phase Carbon Steel

Corrosion behavior of dual-phase carbon steel composed of ferrite and martensite in  $0.1 \text{ mol dm}^{-3}$  sulfuric acid was investigated by both macro- and micro-electrochemical methods. The dual-phase steel corrodes in the acid non-uniformly due to galvanic coupling between its microstructures as well as general corrosion. Hydrogen evolution reaction on martensitic microstructures accelerates to two to three times the corrosion of ferritic microstructures, though martensitic microstructures corrode by itself in the acid.

### (3) Fabrication of Multichannel Microelectrode-array and Its Application

Scanning probe technique such as an SECM enables to visualize the electrochemical activity on a specimen electrode. However it is not suitable to pursue 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 tentatively by using photolithography and electroless plating of nickel or copper. Multi-channels array structure with a diameter of 100  $\mu\text{m}$  successfully showed a microelectrochemical behavior, in which a mass-transfer process becomes characteristic. In the application to air-solution-electrodes interface, non-uniform distribution of dissolved oxygen reduction was obtained.

### (4) *In-situ* observation of passive surface by using an ellipso-microscope

The surface of polycrystalline titanium polarized anodically in 0.05 mol  $\text{dm}^{-3}$  sulphuric acid was monitored using an ellipso-microscope. During the dynamic polarization, the initial null-condition of PCSA optics was gradually unadapted due to formation of the anodic oxide film on the surface. An *in-situ* monitoring using the ellipso-microscope revealed that the film growth rate was dependent on the crystallographic orientation of the substrate. The breakdown of the film induced by addition of bromide ions to the solution was also monitored using the microscope. Prior to the film breakdown, the surface was partially regressed the null-condition with flowing a slightly large anodic current, indicating that the film degradation occurred electrochemically due to formation of bromoxide or something containing bromine. The film degradation tended to occur at the surface covered with a thinner oxide film.

### (5) Microelectrochemical Visualization of Hydrogen Penetrated through Carbon Steel Sheet

In order to avoid hydrogen embrittlement of carbon steel sheet, basic research for mechanism and kinetics of hydrogen penetration is necessary. Microelectrode technique was applied to so-called Devanathan method, in which two electrochemical cells were employed to generate hydrogen on one side of the sheet and to detect hydrogen on the other side. An appropriate electrochemical condition of the microelectrode to visualize the hydrogen detection has been investigated.

### Other Activities

In August, Dr. Koji Fushimi and Mr. Yu Takabatake attended to 9th International Symposium on Electrochemical Micro & Nanosystem Technology, Linz, Austria.

Dr. K. Fushimi presented the keynote lecture entitled “Micro-electrode techniques for corrosion analyses”. Mr. Y. Takabatake presented the paper entitled “Grain-dependent Passivity of Iron in Sulphuric Acid Using Micro-capillary Cell” and won the poster award. Dr. K. Fushimi and Mr. Yu Takabatake also attended to the 63rd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic, and presented the papers entitled “Growth and Breakdown of Anodic Oxide Film on Titanium Observed by Ellipsometric Microscopy” and “Stability of Passive State of Iron Single Grains in Sulphuric Acid Measured by a Micro-capillary-cell”, respectively. In December, Mr. Y. Takabatake attended to the Challenges in Advanced Chemistry of Asia, 2012 HU-NU-SNU-NIMS/MANA Joint Symposium, Sapporo, Japan, and presented the paper entitled “Active and Passive State of Iron in Sulfuric Acid Measured by a Micro-capillary-cell”.

### **Presentations (international symposia)**

T. Ohkubo, T. Nakanishi, K. Fushimi, Y. Hasegawa; Luminescent Eu(III) complex with asymmetric coordination structure by monodentate phosphine oxide, 19th International SPACC symposium, The society of pure and applied coordination chemistry, Sapporo, August 3-4.

Y. Suzuki, Y. Doi, Y. Hinatsu, H. Ito, T. Nakanishi, K. Fushimi, Y. Hasegawa; Magneto-optical properties of Tb(III) clusters, 19th International SPACC symposium, The society of pure and applied coordination chemistry, Sapporo, August 3-4.

K. Fushimi, Y. Takabatake, T. Nakanishi, Y. Hasegawa; Micro-electrode techniques for corrosion analyses, 9th International Symposium on Electrochemical Micro & Nanosystem Technology, Linz, Austria, August 15-17.

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa; Grain-dependent Passivity of Iron in Sulphuric Acid Using Micro-capillary Cell, 9th International Symposium on Electrochemical Micro & Nanosystem Technology, Linz, Austria, August 15-17.

K. Fushimi, K. Kurauchi, T. Nakanishi, Y. Hasegawa, T. Ohtsuka; Growth and Breakdown of Anodic Oxide Film on Titanium Observed by Ellipsometric

Microscopy, 63nd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic, August 19–24.

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa; Stability of Passive State of Iron Single Grains in Sulphuric Acid Measured by a Micro-capillary-cell, 63nd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic, August 19–24.

M. Sakairi, T. Yamaguchi, T. Murata, K. Fushimi, Formation of area and thickness controlled porous type aluminum anodic oxide films by Sf-MDC, PRiME2012 Honolulu.

Yu Takabatake, Koji Fushimi, Takayuki Nakanishi, and Yasuchika Hasegawa , "Active and Passive State of Iron in Sulfuric Acid Measured by a Micro-capillary-cell", Challenges in Advanced Chemistry of Asia, 2012 HU-NU-SNU-NIMS/MANA Joint Symposium, Sapporo, December 6-7.

Akira Kawashima, Takayuki Nakanishi, Koji Fushimi, and Yasuchika Hasegawa, "EuS Nano-assembles Attached with Naphthalenedithiols", Challenges in Advanced Chemistry of Asia, 2012 HU-NU-SNU-NIMS/MANA Joint Symposium, Sapporo, December 6-7.

Kohei Miyata, Takayuki Nakanishi, Atsushi Kobayashi, Masako Kato, Koji Fushimi, and Yasuchika Hasegawa, "Luminescence properties of lanthanide coordinantion polymers with 3-D network structures", Challenges in Advanced Chemistry of Asia, 2012 HU-NU-SNU-NIMS/MANA Joint Symposium, Sapporo, December 6-7.



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Mr. Zheng Meng got his PhD degree on March 2012 and joined institute of oceanology, Chinese academy of science, Qingdao China. Dr. Ningshen is staying our group as JSPS research fellow and USTB master course student Miss Yang Yang (USTB) stay our group from October to March as internship student. Research work of our group directs toward 1) formation of composite oxide films for dielectric materials by anodizing and LPD, 2) reaction size reducing of solution flow type micro-droplet cell and its application, 3) development of micro electrochemical technique for detection of permeated hydrogen formed during corrosion, 4) effect of metal cations on corrosion behavior of aluminum alloys in model tap water, 5) Corrosion behavior of metals in nuclear reprocessing plant environments, 6) formation of hydrophobic porous alumina films by desiccation treatment and these corrosion resistance, and 7) effect of  $\text{CH}_3\text{COONa}$  concentration on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments.

The topics of investigation are in the following:

(1) Formation of novel of oxide film for dielectric materials and anticorrosion films by anodizing and LPD

As NaOH used to control pH of the Liquid Phase Deposition treatment (LPD), LPD and anodizing process can form  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite layer and it shows very high

capacitance. However, NaF layer also deposited on the substrate, and this layer was expected to reduce the phase shift. Therefore, KOH was alternatively used. The effect of KOH addition in solution was investigated. The film formation rate significantly reduced, however, for longer immersion and anodizing makes it possible to form  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite layer. Because of very thin composite layer, not high capacitance was observed.

(2) Reaction size reducing of solution flow type micro-droplet cell and its application

The used co-axial solution flow type micro-droplet cell can anodizing locally, however, reducing the width of the line is a huge demand for apply nano-size electrochemistry. The resin sealed Pt wire 50  $\mu\text{m}$  in diameter was used. The size change by resin sealing was investigated by line anodizing. The current during constant voltage anodizing reduced about 20 %, and the width also reduce about 20 %. The sealing do not any other influence on anodic oxide film formation.

(3) Development of micro electrochemical technique for detection of permeated hydrogen formed during corrosion

Permeated hydrogen shows very important role in hydrogen embrittlement, however, traditional electrochemical cell technique is not suitable for detection of hydrogen generated corrosion at damaged area of coated steels. Using developed cell, the hydrogen permeation current and rest potential during wet and dry cycle corrosion tests at 21 %RH can be simultaneously measured. As drying the placed solution, hydrogen permeation currents returned to same value of the current before placing the solutions. The amount of permeated hydrogen from unit area of scratch is independent of its size.

(4) Effect of metal cations on corrosion behavior of aluminum alloys in model tap water

The corrosion rate of aluminum alloy in model tap water is affected by kind of metal cation in the media. It has been reported that the effect of metal cation on corrosion rate can be explained by metal cation hardness which based on the hard and soft acid and base, HSAB, concept. However, previous research could not avoid corrosion of aluminum because solution contained very low chloride ions. Therefore, sulfate was used as source of metal cations. The peak current of active dissolution and passive current decreases with increasing metal cation hardness. From XPS analysis, hard metal cations are incorporated

in passive oxide film. This incorporation of metal cation into the oxide film may increase strength or reduce defect in the oxide film.

#### (5) Corrosion behavior of metals in nuclear reprocessing plant environments

The main objective of present research work focuses on material issues for spent nuclear fuel reprocessing plant. The aim is to provide better insights about the corrosion reliability of 9-15 %Cr ODS alloys under different nuclear reprocessing environments by micro, surface analytical, mechanical, imaging and electrochemical techniques. The nitric acid concentration impacts the corrosion behavior differently. The X-ray photoelectron spectroscopy study of the oxide formed is composed mainly of  $\text{Fe}_2\text{O}_3$  along with  $\text{Cr}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . The sputter depth profiles of the passive film formed appears different depending on alloy composition and nitric acid concentration. However, all the investigated ODS steels do not show any general or intergranular corrosion attack thereby revealing good resistance to nitric acid in the studied concentrations of up to 9  $\text{HNO}_3$   $\text{kmol m}^{-3}$ . From a practical point of view, this may be pertinent to the structural materials to be used in a nuclear reprocessing plant.

In the solutions without chloride, all the investigated steels exhibited wider passive range and higher breakdown potential. However, low pitting corrosion resistance of both steels in chloride solutions was attributable due to the role of  $\text{Cl}^-$  and microstructural inhomogeneity. XPS analysis of the passive oxide film reveals the existence of the layers of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , and in 9-15 %Cr ODS steel along with  $\text{Y}_2\text{O}_3$ . The SEM morphology of corrosion attack shows severe pitting corrosion attack in both the alloys in chloride solutions.

#### (6) Formation of hydrophobic porous alumina films by desiccation treatment and these corrosion resistance

Diminishing surface wettability is an effective method to improve corrosion resistance of aluminum. Various techniques for preparing hydrophobic surface have been reported, most of which use organic coating as the final step. It has been reported that porous type anodic oxide film formation and desiccation treatment makes it possible to increase contact angle. The effect of anodizing time, length of pore, on water contact angle and corrosion resistance were investigated. The contact angle increased from 10 degree (without desiccation) to about 80 degree (with desiccation). From potentiodynamic polarization measurements, pitting potential and passive current decrease with anodizing and especially longer anodizing. The passive current suppress more with desiccation.

(7) Effect of  $\text{CH}_3\text{COONa}$  concentration on oxide film structure and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments.

The effect of acetate ions on structure of surface oxide films and corrosion behavior by X-ray photon spectroscopy (XPS) and electrochemical techniques. Two different C content (0.2 % and 0.02%) 13 % Cr stainless steels were used as samples, and 25 % NaCl with 0 to 40.0 g/L  $\text{CH}_3\text{COONa}$  at different temperature were used as model environments. From polarization measurements, pitting potential decreases in every condition with increasing  $\text{CH}_3\text{COONa}$  concentration, however, more addition of the  $\text{CH}_3\text{COONa}$ , pitting potential increases with increasing the concentration. From XPS analysis, independent of C content in the substrate, intensity ratio of  $\text{Fe}^0$  increases with increasing  $\text{CH}_3\text{COONa}$  concentration, while intensity ratio of  $\text{Cr}^0$  does not change with  $\text{CH}_3\text{COONa}$  concentration. The intensity ratio of  $\text{O}^{2-}$  also increases with increasing  $\text{CH}_3\text{COONa}$  concentration.

#### Other activities

From February to March, Miss. Kikkawa stayed as an internship student in Fontana Corrosion Center, The Ohio State University, Ohio USA under supervision of Prof. Gerald S. Frankel.

In March Dr. Ningshen and Mr. Zheng attended 6th Japan-China Joint Seminar on Marine Corrosion at Tokyo Japan. Dr. Ningshen presented a paper entitled "Corrosion Resistance and Passive Film Characterization of 9Cr Oxide Dispersion Strengthened Steel in Acidic and Chloride Environment" and Mr. Zheng presented a paper entitled "Porous structure control of hydrophobic aluminum oxide film and its corrosion".

In May, Assoc. of Prof. Sakairi attended ASST6 at Sorrento Italy and presented two papers entitled "Formation of alumina films with nano-dots structures by liquid phase deposition and anodizing" and "Analysis of surface film and morphology of 3003 aluminum alloy after immersion in different cation contained model tap waters".

In June, Assoc. Prof. Sakairi invited NIMS Conference 2012 at Tsukuba, Japan and presented a paper entitled "Corrosion behavior of 11 mass% Cr F/M steel and 15 mass% Cr ODS steel in high acid concentration solutions".

In September, Assoc. Prof. Sakairi and Mr. Takagi attended HU-AGH symposium at Krakow Poland. Assoc. Prof. Sakairi presented a papers entitled "Effect of metal cations on oxide film structure and corrosion behavior of

aluminum alloy" and Mr. Takagi presented a paper entitled "Development of electrochemical hydrogen permeation  $\mu$ -cell and its application to atmospheric corrosion at scratch of zinc coated steels".

In September, Assoc. Prof. Sakairi attended EUROCORN2012 at Istanbul Turkey presented a paper entitled "Evaluation of cations effect on corrosion of Al in model tap water by HSAB theory".

In October, Dr. Ningshen attended NuMat 2012 at Osaka Japan and presented a paper entitled "Corrosion Behavior of Ferritic/Martensitic Steel and 9 -15% Cr ODS Steels in Nitric Acid Media".

In October Assoc. Prof. Sakairi attended 223th ECS meeting at Hawaii USA and presented two papers entitled "Formation of area and thickness controlled porous type aluminum anodic oxide films by Sf-MDC" and "Effect of halogen ions and inhibitors on corrosion behavior of 13 Cr stainless steel in packer fluid".

In October Assoc. Prof. Sakairi attended The 16th APCCC at Kaohsiung, Taiwan and presented a paper entitled "Effect of acetate ions on polarization behavior of low C -13%Cr stainless steel in acid NaCl solutions".

In December Assoc. Prof. Sakairi attended

## **Facilities and Capabilities**

AFM: SII SMP AFM with solution cell.

Confocal scanning laser microscope Laser Tech. Co. ISA-21

Pulse Laser system: 10Hz and 50 Hz pulsed Nd-YAG Laser with electric XYZ stage

Electrochemical AC Impedance: NF Circuit Design 5095 FRA equipped with potentiostat.

Co-axial solution flow type micro droplet cell

Multi thin layer electro deposition system

## **Presentations**

Corrosion behavior of 13Cr stainless steel in acid high concentration NaCl solutions, A. Kikkawa, M. Sakairi and S. Hasizume, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, Jan., 2012.

Structure change of Ni-Al micro-channel lining layer with alkaline reaching treatment of Ni-Al, Y. Saito, T. Ohmi, M. Sakairi and M. Iguchi, *ibid.*

Effect of metal cations in model tap water on oxide film structure of A3003, K. Otani, M. Sakairi, A. Kaneko, Y. Seki and D. Nagasawa, The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2012.

Simultaneous detection of rest potential and hydrogen permeation current during corrosion of Zn coated steel, S. Takagi and M. Sakairi, *ibid.*

Corrosion Resistance and Passive Film Characterization of 9Cr Oxide Dispersion Strengthened Steel in Acidic and Chloride Environment, S. Ningshena, M. Sakairi K. Suzuki and S. Ukai, 6th Japan-China Joint Seminar on Marine Corrosion, March, Tokyo, 6th Japan-China Joint Seminar on Marine Corrosion

Porous structure control of hydrophobic aluminum oxide film and its corrosion protection study, M. Zheng, M. Sakairi and H. Jha, *ibid*

Effect of metal cations on corrosion behavior of Al in fresh water, M. Sakairi, K. Otani, A. Kaneko, Y. Seki and D. Nagasawa, 148th spring meeting of Jpn. Inst. Metals, Yokohama, March, 2012.

Anodizing of plane lining layer formed with sacrificial core method, M. Ishida, T. Ohmi, M. Sakairi and M. Iguchi, *ibid.*

Formation of high dielectric film for Al electrolytic capacitor by LPD and anodizing, M. Sakairi, T. Sasaki, R. Fujita and S. Nagata, The 79th Meeting of the Electrochem. Soc. of Jpn., Hamamatsu, March, 2012.

Simultaneous hydrogen and rest potential measurement during wet/dry corrosion at scratch on zinc coated steel, M. Sakairi and S. Takagi, Zairyo-to-Kankyo 2012, Tokyo, April, 2012.

Change of hydrogen intruder the Zn coated steel during wet/dry corrosion tests, S. Takagi and M. Sakairi, *ibid.*

Oxide film structure formed on Ni base alloys in PWR environment, Y. Hamaguchi,

A. Hyono, T. Ohtuka, M. Sakairi, G. Nakayama and Y. Sakakibara, *ibid.*

Effect of metal cation on corrosion rate of aluminum alloy in model tap water, M. Sakairi and K. Otani, The 122th meeting of Light metal soc., May, Fukuoka, 2012

Formation of alumina films with nano-dots structures by liquid phase deposition and anodizing, M. Sakairi, R. Fujita, H. Jha and T. Kikuchi, ASST6, May Sorrento, Italy, 2012.

Analysis of surface film and morphology of 3003 aluminum alloy after immersion in different cation contained model tap waters, M. Sakairi, K. Otani, A. Kaneko, Y. Seki and D. Nagasawa, *ibid.*

The Surface modification of Anodized Titanium by Multi-Walled Carbon Nanotubes, S. Inoue, M. Uo, M. Sakairi, E. Hirata, M. Lee, T. Bae, T. Akasaka, S. Abe, F. Watari, A. Yokoyama, 9th World Biomaterials Congress, China, June, 2012.

Corrosion behavior of 11 mass% Cr F/M steel and 15 mass% Cr ODS steel in high acid concentration solutions, M. Sakairi, S. Ningshen, K. Suzuki and S. Ukai, NIMS conference 2012, Tsukuba, June, 2012.

Effect of substrate temperature and concentration of solution on local PAOF formation by Sf-MDC, T. Yamaguchi, M. Sakairi and K. Fushimi, Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Asahikawa, July, 2012.

Formation of high dielectric oxide film on aluminum by LPD and anodizing, T. Sasaki and M. Sakairi, *ibid.*

Detection of hydrogen formed during wet/dry corrosion tests of Zn coated steel, S. Takagi and M. Sakairi, The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, July, 2012.

Effect of metal cations on oxide film structure and corrosion behavior of aluminum alloy, M. Sakairi, Polish-Japanese Seminar (HU-AGH seminar), Krakow, Poland, September, 2012.

Development of electrochemical hydrogen permeation  $\mu$ -cell and its application to atmospheric corrosion at scratch of zinc coated steels, M. Takagi and M. Sakairi, *ibid.*

Evaluation of cations effect on corrosion of Al in model tap water by HSAB theory, M. Sakairi, K. Otani, A. Kaneko, Y. Seki and D. Nagasawa, EUROCORR2012, Istanbul Turkey, September, 2012.

Difference of UPD of Pb on Ni by solution composition, M. Seo, K. Fushimi, M. Sakairi and T. Nakayama and H. Habazaki, Discussion meeting of Ziryto-to-Kankyo, Asahikawa, September, 2012.

Injection behavior of hydrogen at defect of Zn coated steel by  $\mu$ -electrochemical cell, S. Takagi and M. Sakairi, *ibid.*

Formation of thin anodic oxide film for Al electrolytic capacitor by LPD and anodizing, T. Sasaki, M. Sakairi and S. Nagata, The 126th meeting of Surf. Fin. Soc. JPN, Muroran, September, 2012.

Formation of PAOF locally by Sf-MDC, T. Yamaguchi, M. Sakairi, K. Fushimi, *ibid.*

Local surface modification by Sf-MDC, M. Sakairi, *ibid.*

Corrosion resistance of OSD steels in acid media, M. Sakairi, S. Ningshen, K. Suzuki and S. Ukai, The 151th meeting of Matsuyama, Jpn. Inst. Metals, September, 2012.

Corrosion Behavior of Ferritic/Martensitic Steel and 9 -15% Cr ODS Steels in Nitric Acid Media, S. Ningshen, M. Sakairi, K. Suzuki and S. Ukai, NuMat 2012, Osaka, October, 2012

Effect of acetate ions on polarization behavior of low C -13%Cr stainless steel in acid NaCl solutions, M. Sakairi, J. Tatehara, A. Kikawa and S. Hasizume, The 16th APCCC12, Kaohsiung, Taiwan October, 2012.

Formation of area and thickness controlled porous type aluminum anodic oxide



films by Sf-MDC, M. Sakairi, T. Yamaguchi, T. Murata and K. Fushimi, 223th ECS meeting, Hawaii, October, 2012.

Effect of halogen ions and inhibitors on corrosion behavior of 13 Cr stainless steel in packer fluid, M. Sakairi, R. Fujita, A. Kageyama, M. Kimurta and Y. Miyata, *ibid.*

Fabrication of Flexible Alumina Microlens Array by Laser Irradiation and Aluminum Anodizing, T. Kikuchi, Y. Wachi, T. Takahashi, M. Sakairi, and R. Suzuki, *ibid.*

The effects of the coating of anodized titanium with multi-walled carbon nanotubes on bone formation, S. Inoue, M. Uo, M. Sakairia, E. Hirataa, M. H. Lee, T. S. Bae, T. Akasakaa, F. Wataria and A. Yokoyamaa, Bioceramics-24, Fukuoka, October, 2012.

Alkali Leaching of Cu-Al Alloy Microchannel Lining Layer, A. Maruyama, T. Ohomi, M. Sakairi and M. Iguchi, 7th ISEM, Taipei, Taiwan, November, 2012.

Formation of Nanoporous Structures on Al-Zn Alloy Lining Layers by Anodic Oxidation, M. Ishida, T. Ohmi, M. Sakairi and M. Iguchi, *ibid*

Hydrogen entry behavior of steels by  $\mu$ -droplet cell, S. Takagi and M. Sakairi, Corrosion Dream 2012, Tokyo, December, 2012.

Corrosion of Oxide Dispersion Strengthened(ODS) Ferritic Steels, M. Sakairi, S. Ningshen, K. Suzuki and S. Ukai, The HU-SNU Joint Symposium on Materials Science and Engineering, Sapporo, December, 2012.

## AFFILIATE MEMBER

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The research activities of the laboratory are directed to the high-temperature oxidation and corrosion. Our particular interests are an understanding of the mechanism of the high temperature corrosion and oxidation of metals such as superalloys, intermetallic compounds, Fe or Ni-based alloys, and steels.

Current topics on research are in the following:

(1) Phase transformation of  $Al_2O_3$  scale formed on Fe and/or Ni based oxidation resistant alloys

Metastable to stable  $\alpha-Al_2O_3$  transformation is one of the critical issues to improve the oxidation resistance of  $Al_2O_3$  scale forming alloys and coatings. In order to control the phase transformation of  $Al_2O_3$ , the effect of Fe, Ni, Cr in alloys on the phase transformation of  $Al_2O_3$  scale are being investigated. Fe and Cr accelerated the transformation, but Ni delayed the transformation to  $\alpha-Al_2O_3$ . In-situ X-ray diffraction studies of reaction products, which formed during an initial transient stage of oxidation including heating and following isothermal oxidation stages, revealed that the oxides having isomorphous structure with  $\alpha-Al_2O_3$  was found to accelerate the transformation.

(2) Phase transformation of Fe oxide scale formed on steels under low  $P_{O_2}$

The microstructure and mechanical and chemical properties of Fe-oxide scale formed on hot rolled strips during a hot-rolling affect the surface quality of strips. Since FeO scale transforms to Fe and  $Fe_3O_4$  due to the eutectoid reaction below the temperature at 570°C, development of the microstructure of oxide scale is strongly affected by the transformation of FeO. Our previous studies indicated that super-saturation of Fe in FeO scale has important role for the eutectoid reaction of

FeO, and super-saturation of FeO is caused by Fe rejection due to the growth of outer Fe<sub>3</sub>O<sub>4</sub> layer and pro-eutectoid Fe<sub>3</sub>O<sub>4</sub> precipitation. In order to confirm this mechanism, the phase transformation behaviors of FeO under low P<sub>O2</sub> atmospheres are being investigated. The start of the phase transformation of FeO delayed under the low P<sub>O2</sub> atmospheres due to delayed formation of pro-eutectoid Fe<sub>3</sub>O<sub>4</sub> precipitates, but it completed with shorter transformation time.

### (3) Effect of oxygen on formation behavior of Al<sub>2</sub>O<sub>3</sub> scale on Nb-based alloys

Nb-based alloy is one of the candidates for next generation superalloy. However oxidation resistance of Nb-based alloys are very poor. One of the reasons of their poor oxidation resistance is low stability of protective oxide scale on the alloys due to higher oxygen solubility in Nb alloys. In order to improve the oxidation resistance of Nb-based alloys, Nb-O based alloys are proposed in this study. Protective Al<sub>2</sub>O<sub>3</sub> scale was developed on Nb based alloys with the two-step oxygen and aluminium diffusion treatment. This protective Al<sub>2</sub>O<sub>3</sub> scale could protect the alloy substrate for short-term oxidation in air, but further improvement of the stability of Al<sub>2</sub>O<sub>3</sub> scale on Nb-based alloys is still necessary for long-term oxidation resistance.

### (4) Oxidation and carburization behavior of Fe-low Cr alloys

Fe-low Cr alloys are widely used as boiler tube materials of fossil fuel combustion power generation plants. In order to decrease CO<sub>2</sub> emission from fossil fuel power plants, CO<sub>2</sub> capturing technique by oxyfuel combustion is being proposed recently. Under the oxyfuel combustion, materials in a boiler are exposed in atmospheres with higher CO<sub>2</sub> content. Therefore evaluation of oxidation behavior of Fe-low Cr alloys in CO<sub>2</sub> is necessary. Internal carbide precipitates was formed under the external oxide scale when Fe-low Cr alloy was oxidized in CO<sub>2</sub> at 700°C. Formation of internal carbide caused breakaway of protective Cr<sub>2</sub>O<sub>3</sub> scale.

### (5) Internal oxidation of ternary alloys

Internal oxidation and transition to external oxide scale formation are one of the most important topics in high temperature oxidation of alloys. There are many studies of internal oxidation in binary systems, however; only limited studies have been conducted in ternary systems. In this study, the effect of third elements on internal oxidation of Fe-Si alloys is being investigated. Growth kinetics of internal oxidation of Si in Fe-Si-X (X=P, Ti, Al) alloys decreased with the addition of P and Ti, but no apparent effect of Al was observed. Based on the TEM analysis, internal precipitates of TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> were found to be nucleation sites for internal

amorphous SiO<sub>2</sub> precipitation. Different precipitate morphology of internal precipitates of third element oxide may affect the oxidation kinetics.

## Presentations

Formation of Al<sub>2</sub>O<sub>3</sub> scale on Nb-O alloy by Al diffusion process: R. Yamagata, S. Hayashi, S. Ukai, and T. Narita: The Spring Meeting of Jpn. Inst. Metals, Yokohama, Japan, May, 2012.

Phase transformation behavior of Al<sub>2</sub>O<sub>3</sub> scale formed on Fe-Al alloys: Y. Takada, S. Hayashi, and S. Ukai: The Spring Meeting of Jpn. Inst. Metals, Yokohama, Japan, May, 2012.

Effect of Ni on the phase transformation of Al<sub>2</sub>O<sub>3</sub> scale: S. Hayashi, A. Yamauchi, I. Saeki, Y. Nishiyama, T. Doi, S. Kyo, M. Sato: The Spring Meeting of Jpn. Inst. Metals, Yokohama, Japan, May, 2012.

Effect of Ni on high temperature oxidation behavior of Fe-42.5Al alloy: S. Takada, S. Hayashi, and S. Ukai: 59<sup>th</sup> Japan Conference on Materials and Environments, Sep. Asahikawa, Japan, 2012.

Improvement of high-temperature oxidation resistance of Ni-Al alloy using nano-composite Ni-Fe<sub>2</sub>O<sub>3</sub> seeding layer: A. Shaaban, S. Hayashi, K. Azumi, 59<sup>th</sup> Japan Conference on Materials and Environments, Sep. Asahikawa, Japan, 2012.

Effect of Mn on phase transformation of oxide scale formed on Fe-Mn alloys: S. Yoneda, S. Hayashi, Y. Kodo, H. Tanei, and S. Ukai: 59<sup>th</sup> Japan Conference on Materials and Environments, Sep. Asahikawa, Japan, 2012.

Oxidation behavior of Nb-Al-Re-O alloy at 1200°C in air: R. Yamagata, S. Hayashi, S. Ukai, and T. Nagata: 59<sup>th</sup> Japan Conference on Materials and Environments, Sep. Asahikawa, Japan, 2012.

Effect of P on internal oxidation of Fe-Si-P alloys: F. Tsutsumi, S. Hayashi, N. Sugiura, and S. Ukai: 59<sup>th</sup> Japan Conference on Materials and Environments, Sep. Asahikawa, Japan, 2012.

Oxidation behavior of Fe-9Cr steel in CO<sub>2</sub>: K. Kaya, S. Hayashi, and S. Ukai; 59<sup>th</sup> Japan Conference on Materials and Environments, Sep. Asahikawa, Japan, 2012.

Carburization-Oxidation behavior of Hastelloy-X: S. Hayashi, S. Ukai, C. Matsukawa, K. Kaya, and H. Yakuwa: JSPS 123 committee research workshop, Nov. 2012.

Cyclic carburization-oxidation behavior of Hastelloy-X at 1000°C: S. Hayashi, C. Matsukawa, H. Yakuwa, T. Narita, T. Kishikawa, and S. Ukai: HTCPM2012, France, May 2012.

High temperature corrosion of Hastelloy-X in various carbon containing atmospheres: S. Hayashi, C. Matsukawa, K. Kaya, and S. Ukai: EFC workshop, Frankfurt Germany, Sep. 2012.



## **ABSTRACT of PUBLICATIONS**





## Potential Modulation Reflectance of Passivated Type 304 Stainless Steel in Sulfuric Acid Solution

T. Ohtsuka, A. Hyono, and Y. Sasaki

Electrochim. Acta, **60**, 384-391 (2012)

Potential modulation reflectance (PMR) was applied to passivated type 304 stainless steel covered by a passive oxide film in 0.1 mol dm<sup>-3</sup> sulfuric acid solution. The ellipsometry measurements showed that the passive oxide film was 1.0 nm thick at the beginning of passivation at 0.1 V vs. Ag/ AgCl and increased to 1.8 nm with potential at 0.9 V in the transpassive region. Under positive bias, the signal intensity of PMR was proportional to the capacitance of the space charge formed in the *n*-type semiconducting passive oxide. The Mott-Schottky type plot was applicable to PMR as well as capacitance. From the plots the oxide film was found to behave as an *n*-type semiconducting layer. A threshold photon energy of 2.4 eV in the PMR–wavelength relation may correspond to the optical absorption edge of the passive oxide.

## Polypyrrole Film on 55% Al-Zn-coated Steel for Corrosion Prevention

H. Ryu, Nan Sheng, T. Ohtsuka, S. Fujita and Hiroshi Kajiyama

Corrosion Science, **56**, 67-77 (2012)

For corrosion protection of 55% Al–Zn-coated steel, a dense polypyrrole (PPy) film is electrochemically formed on 55% Al–Zn-coated steel in an acidic tartrate solution under constant current control. The film potentially consists of an inner layer of aluminium and/or zinc oxide and an outer PPy layer doped with tartrate anions. The PPy layer can maintain passivation of 55% Al–Zn-coated steel in a 3.5 wt.% NaCl aqueous solution and protected the steel for several hours. The doping of molybdate anions into the PPy–tartrate film greatly improved the film's protective properties.

## Corrosion Protection of Steels by Conducting Polymer Coating

Toshiaki Ohtsuka

International Journal of Corrosion, 2012, Article ID 915090 (2012):

The corrosion protection of steels by conducting polymer coating is reviewed. The conducting polymer such as polyaniline, polypyrrole, and polythiophen works as a strong oxidant to the steel, inducing the potential shift to the noble direction. The strongly oxidative conducting polymer facilitates the steel to be passivated. A bilayered PPy film was designed for the effective corrosion protection. It consisted of the inner layer in which phosphomolybdate ion,  $\text{PMo}_{12}\text{O}_{40}^{3-}$  (PMo) was doped and the outer layer in which dodecylsulfate ion (DoS) was doped. The inner layer stabilized the passive oxide and the outer possessed anionic perm-selectivity to inhibit the aggressive anions such as chloride from penetrating through the PPy film to the substrate steel. By the bilayered PPy film, the steel was kept passive for about 200 h in 3.5% sodium chloride solution without formation of corrosion products.

## Corrosion Products of Zinc and their Protection Property

Toshiaki Ohstuka

Report of Corrosion and Protection Committee, The Society of Materials Sci.,  
Japan, No. 284, vol. 50, Part 4, 1-8 (2012)

Zinc and its alloys were effectively used for sacrificed anode. In the presence of NaCl, the corrosion products in zinc under atmospheric exposure consist of ZnO,  $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4\text{H}_2\text{O}$ ,  $\text{ZnCO}_3[\text{Zn}(\text{OH})_2]_3$ . The corrosion rate of zinc under the atmospheric condition was by (1/10) smaller than that of iron. The reason for the small rate is due that the counter cathodic reactions such as oxygen reduction and hydrogen evolution on zinc are smaller than those on iron. The corrosion products induce further protection of the base metals. (Japanese)

## **Corrosion of Steels in Aqueous Solution**

Toshiaki Ohtsuka

Ferumu (Bull. Iron and Steel Institute of Japan), **17**, 220-225 (2012)

Basic electrochemical mechanism was reviewed. The following contents were included: (1) Electrochemical cell model, (2) Mixed potential and corrosion potential, (3) Electrochemical equilibrium and corrosion, (4) Cathodic protection and anodic protection, (5) Corrosion rate of steel in aqueous solution, (6) Role of corrosion rust of iron in corrosion, and (7) Corrosion of low-alloy steels and stainless steels. (Japanese)

## **Passive Oxide Films on Iron by In-situ Detection of Optical Techniques**

T. Ohtsuka

Modern Aspects of Electrochemistry 47- Progress in Corrosion Science and Engineering II, Ed. By Su-Il Pyun and J.-W. Lee, Springer, 183-241 (2012)

Various optical techniques and the results of passive oxide film on iron measured by the techniques were reviewed. For the optical techniques, following techniques are introduced. (1) Ellispometry, (2) Raman spectroscopy, and (3) AC techniques including potential modulation reflectance, From ellispometry, the linear growth of the passive oxide film with increase of potential was found. From the Raman spectroscopy, the composition of the oxide was found to be  $g\text{-Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ . From the AC technique, the oxide film was found to behave as n-type semiconducting electrode.

## **Preparation of Conducting Poly-pyrrole Layer on Zinc Coated Mg Alloy of AZ91D for Corrosion Protection**

N. Sheng and T. Ohtsuka

Progress in Organic Coatings, **75**, 59-64 (2012)

Conducting polypyrrole (PPy) film was successfully prepared on the zinc coated magnesium alloy of AZ91D by electrochemical oxidation under constant current control in sodium tartrate aqueous solution. The oxidation was started from the formation of zinc oxide and zinc tartrate, followed by PPy electropolymerization. Surface morphology and the layer structure were analyzed by using scanning electron spectroscopy (SEM) and energy dispersive spectroscopy (EDS), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The PPy coating exhibited protection properties of zinc coated magnesium alloy against corrosion in sodium chloride aqueous solution. The PPy coating is assumed to enhance the open circuit potential of zinc coated alloy and cause the alloy to be passivated.

### **Al Electroplating on the AZ121 Mg Alloy in an EMIC- $\text{AlCl}_3$ Ionic Liquid Containing Ethylene Glycol**

Mikito Ueda, Shizuka Hariyama, and Toshiaki Ohtsuka

Journal of Solid State Electrochemistry, **16**, 3423-3427 (2012)

To improve the corrosion resistance of Mg alloys, an Al layer was electrodeposited on the Mg surface from an ionic liquid of 1-ethyl-3-methylimidazolium chloride and aluminum chloride at 283 K. A smooth surfaced Al electrodeposit can be electroplated in the  $\text{AlCl}_3$ -EMIC ionic liquid by pulse electrolysis at 6.7 Hz and a duty ratio of 0.67. A denser and flatter Al layer was successfully electroplated on AZ121 substrate at the lower temperature of 283 K in a  $\text{AlCl}_3$ -EMIC ionic liquid with 0.1 M ethylene glycol added.

### **Diffusion of Tl Ions into Glass Treated by Molten Salt Ion Exchange and Hydrogen Reduction**

Mikito Ueda, Hajime Matsunaga, Toshiaki Ohtsuka, Toshiharu Yamashita

Materials Transactions, **53**, 575-577 (2012)

To investigate the diffusion behavior of Tl ions, glass was immersed in  $\text{TlNO}_3\text{-KNO}_3$  molten salt at 753 K for various lengths of time. The Tl ions embedded in the glass were then reduced to metallic Tl nano-particles by hydrogen at 803 K for 1h. The depth of the ion exchange layer down to about 140  $\mu\text{m}$  in the glass was found to be proportional to a square root of the length of immersion time. It was suggested that the ion exchange process is controlled by the diffusion of Tl ions from the surface to the inside. Reduction of Tl ions to metallic Tl with the hydrogen gas occurred only at the surface down to 4  $\mu\text{m}$ . The concentration profile of the metallic Tl is discussed by nucleation-nucleus growth and the diffusion of Tl ions from deeper areas.

### **Synthesis and Antibacterial Properties of Water-dispersible Silver Nanoparticles Stabilized by Metal–Carbon $\sigma$ -Bonds**

K. Kawai, T. Narushima, K. Kaneko, H. Kawakami, M. Matsumoto, A. Hyono, H. I. Nishihara, and T. Yonezawa

*Applied Surface Science*, **262**, 76-80 (2012)

The synthesis of 4-diazoniumcarboxylbenzene fluoroborate, a new water-soluble stabilizer for metal nanoparticles (NPs), is described. A stable dispersion of Ag NPs in water was successfully produced by a simultaneous aqueous reduction of this diazonium salt and silver nitrate by  $\text{NaBH}_4$ . UV–vis spectra, TEM images, XRD patterns, and XPS spectra of the obtained Ag NPs revealed that they were stabilized by Ag–C  $\sigma$ -bonds. These NPs showed excellent antimicrobial properties against *Staphylococcus aureus*.

### **Percolative Proton Conductivity of Sol–gel Derived Amorphous Aluminosilicate Thin Films**

Y. Aoki, A. Harada, A. Nakao, T. Kunitake and H. Habazaki

Physical Chemistry Chemical Physics, **14**, 2735-2742 (2012)

The finite size effect of proton conductivity of amorphous aluminosilicate thin films,  $a\text{-Al}_n\text{Si}_{1-n}\text{O}_x$  ( $n = 0.07, 0.1, 0.2, 0.3$  and  $0.45$ ), prepared by a sol-gel process was investigated by experimental and numerical techniques. High-resolution TEM clarified that  $a\text{-Al}_n\text{Si}_{1-n}\text{O}_x$  films had the heterogeneous nanoscale microstructures comprised of the ion-conducting, condensed glass microdomain and the poor-conductive, uncondensed glass microdomain.  $\sigma$  of the films with  $n \leq 0.1$  exponentially increased upon decreasing thickness in the sub-100 nm range because the volume fraction of conductive domains was less than the percolation threshold and cluster size scaling of the conductive domain was operative. The numerical simulation suggested that conductance of the condensed domain was higher than that of the uncondensed domain by 2 orders of magnitude. Volume fractions of the condensed domain increased with increasing Al/Si molar ratio and were over the percolation threshold (24.5%) with  $n \geq 0.2$ . However, conductance of the condensed domain decreased with increasing Al/Si ratio with  $n \geq 0.2$  because the aluminosilicate glass framework made of 4-fold-connected  $\text{MO}_4$  tetrahedra was deformed by forming the octahedral  $\text{AlO}_6$  moieties, as checked by Al K-edge XAS. It was found that the optimal Al/Si composition in terms of the conductance of the condensed domain is not in coincidence with that in terms of the average conductivity of the films.

## **Ion Migration and Film Morphologies in Anodic Alumina Films Formed in Selenate Electrolyte**

A. Baron-Wiechec, O. Ekundayo, S.J. Garcia-Vergara, H. Habazaki, H. Liu, P. Skeldon and G.E. Thompson

Journal of the Electrochemical Society, **159**, C312-C317 (2012)

Film morphologies and ionic migration are investigated for anodic oxides formed galvanostatically on electropolished aluminum in selenate electrolyte. Anionic selenium species that migrate at similar to 0.2 to 0.3 times the rate of  $\text{O}^{2-}$  ions were present in barrier films. Further, porous films could be generated by the use of sputtering-deposited aluminum substrates, although the film thickness is limited to

similar to 70 nm. Re-anodizing in pentaborate electrolyte at high efficiency revealed also a cationic selenium species that migrates at similar to 0.6 to 0.7 times the rate of  $\text{Al}^{3+}$  ions, suggesting that the migration of selenium is affected by the morphology and growth mechanism of the film.

## **The Influence of Nitrogen Incorporation on the Optical Properties of Anodic $\text{Ta}_2\text{O}_5$**

F. Di Franco, M. Santamaria, F. Di Quarto, E. Tsuji and H. Habazaki

*Electrochimica Acta*, **59**, 382-386 (2012)

Anodic oxides were grown on sputter-deposited Ta in different aqueous solutions. A photoelectrochemical investigation was performed in order to estimate the band gap of the films as a function of the anodizing bath composition and formation voltage, i.e. thickness. Photoelectrochemical results provided evidence of sub-band gap photocurrent for films formed in a bath containing ammonium ions at pH 9. Elemental depth profiles obtained by glow discharge optical emission spectroscopy revealed the presence of nitrogen species in the outer part of the anodic films, which is bonded to Ta according to XPS analysis. A mechanism of nitrogen incorporation is proposed in order to account for the pH dependence of film composition.

## **Characterization of the Solid State Properties of Anodic Oxides on Magnetron Sputtered Ta, Nb and Ta-Nb Alloys**

F. Di Franco, G. Zampardi, M. Santamaria, F. Di Quarto and H. Habazaki

*Journal of the Electrochemical Society*, **159**, C33-C39 (2012)

Tantalum oxide, niobium oxide and Ta-Nb containing mixed oxides were grown by anodizing sputter-deposited Ta, Nb and Ta-Nb alloys of different compositions. A photoelectrochemical investigation was performed in order to estimate the band gap and the flat band potential of the oxides as a function of their composition. The band gap of the investigated Ta-Nb containing mixed oxides changed

monotonically between those estimated for Ta<sub>2</sub>O<sub>5</sub> (4.1 eV) and Nb<sub>2</sub>O<sub>5</sub> (3.4 eV) and in agreement with a proposed correlation between the Band gap of an oxide and the difference of electronegativity of the oxide constituents. From the differential capacitance curves recorded in a wide range of electrode potential and for several frequencies of the alternative signal, the dielectric constant of the investigated oxides were estimated.

## **Important Role of Nanopore Morphology in Superoleophobic Hierarchical Surfaces**

T. Fujii, H. Sato, E. Tsuji, Y. Aoki and H. Habazaki

Journal of Physical Chemistry C, **116**, 23308-23314 (2012)

This work reports the importance of nanopore morphology in designing super liquid-repellent submicropillar/nanopore hierarchical surfaces. The hierarchical surfaces were fabricated using a combined process of oblique angle sputter deposition of aluminum with subsequent anodizing, and the surfaces were coated with a fluorinated alkyl phosphate layer to reduce the surface energy. The size of the nanopores, the interpore distance, and the porosity of the anodic films on the submicrometer pillars were controlled by varying the anodizing and pore-widening conditions. The present study demonstrates that super liquid repellency can be achieved on intrinsically oleophilic surfaces by introducing hierarchical submicropillar/nanopore morphology even for oils with surface energies as low as similar to 25 mN m<sup>-1</sup>. The porosity in the submicrometer pillars was a key factor in influencing the contact angle hysteresis; higher porosity is needed to reduce the contact angle hysteresis.

## **Formation and Characterization of Wear-resistant PEO Coatings Formed on $\beta$ -titanium Alloy at Different Electrolyte Temperatures**

H. Habazaki, S. Tsunekawa, E. Tsuji and T. Nakayama



Applied Surface Science, **259**, 711-718 (2012)

Plasma electrolytic oxidation of single  $\beta$ -phase Ti–15 mass% V–3 mass% Al–3 mass% Cr–3 mass% Sn (hereafter denoted as Ti–15–3) alloy has been conducted in alkaline aluminate electrolyte at different electrolyte temperatures between 278 and 313 K. The results obtained disclose the highly improved wear resistance of the coatings formed at the lowest temperature of 278 K. The coating formed at this temperature has lower porosity and contains higher concentration of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase in addition to the Al<sub>2</sub>TiO<sub>5</sub> major phase. In contrast, non-uniform coatings are formed at higher temperatures and their porosity is relatively high. Thus, the highest wear resistance of the Ti–15–3 is obtained when the coating is formed at 278 K. Such influence of the electrolyte temperature on the coating morphology and composition is discussed by direct imaging based on direct video imaging data during the coating process.

## Growth and Field Crystallization of Anodic Films on Ta–Nb Alloys

S. Komiyama, E. Tsuji, Y. Aoki, H. Habazaki, M. Santamaria, F. Quarto, P. Skeldon and G.E. Thompson

Journal of Solid State Electrochemistry, **16**, 1595-1604 (2012)

The growth behavior of amorphous anodic films on Ta–Nb solid solution alloys has been investigated over a wide composition range at a constant current density of 50 Am<sup>-2</sup> in 0.1 mol dm<sup>-3</sup> ammonium pentaborate electrolyte. The anodic films consist of two layers, comprising a thin outer Nb<sub>2</sub>O<sub>5</sub> layer and an inner layer consisting of units of Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>. The outer Nb<sub>2</sub>O<sub>5</sub> layer is formed as a consequence of the faster outward migration of Nb<sup>5+</sup> ions, compared with Ta<sup>5+</sup> ions, during film growth under the high electric field. Their relative migration rates are independent of the alloy composition. The formation ratio, density, and capacitance of the films show a linear relation to the alloy composition. The susceptibility of the anodic films to field crystallization during anodizing at constant voltage increases with increasing niobium content of the alloy.

## **Factors Influencing the Growth Behaviour of Nanoporous Anodic Films on Iron under Galvanostatic Anodizing**

Y. Konno, E. Tsuji, P. Skeldon, G.E. Thompson and H. Habazaki

Journal of Solid State Electrochemistry, **16**, 1-10 (2012)

The growth behaviour of nanoporous anodic films on iron during galvanostatic anodizing in ethylene glycol electrolytes containing  $\text{NH}_4\text{F}$  and  $\text{H}_2\text{O}$  is examined at various current densities,  $\text{H}_2\text{O}$  concentrations in electrolytes and temperatures. The film morphology is mainly controlled by the formation voltage, regardless of anodizing conditions. Relatively regular cylindrical pores are formed at formation voltages less than 50 V, while rather disordered pores are formed above 100 V. The decrease in the  $\text{H}_2\text{O}$  concentration suppresses chemical dissolution of anodic films in addition to the increased growth efficiency, resulting in the formation of anodic films with a steady thickness of  $\sim 7 \mu\text{m}$ . The cell size of the anodic films depends upon the  $\text{H}_2\text{O}$  concentration as well as the formation voltage, but not upon the current density. Findings in this study will be useful for controlled growth of the anodic films on iron.

## **Formation of Self-organized Nanoporous Anodic Films on Type 304 Stainless Steel**

K. Kure, Y. Konno, E. Tsuji, P. Skeldon, G.E. Thompson and H. Habazaki

Electrochemistry Communications, **21**, 1-4 (2012)

The formation of self-organized nanoporous anodic films on Type 304 stainless steel in fluoride-containing ethylene glycol electrolyte is reported. A key factor in the formation of the nanoporous anodic films is the water concentration in the electrolyte, which must be  $0.3\text{mol dm}^{-3}$  or less for the present conditions of film formation, although nanoporous anodic films have been formed on iron at higher water concentrations. The films contain relatively high concentrations of iron, chromium, nickel, oxygen and fluorine species distributed throughout the film thicknesses. The fluoride species can be removed by post-annealing in air, which improves the chemical stability of the films without damaging the

nanoporous morphology of the remaining oxide.

## **The Superhydrophobic Properties of Self-organized Microstructured Surfaces Derived from Anodically Oxidized Al/Nb and Al/Ta Metal Layers**

A. Mozalev, H. Habazaki and J. Hubálek

*Electrochimica Acta*, **82**, 90-97 (2012)

Al/Nb and Al/Ta metal layers sputter-deposited onto Si wafers were anodized respectively in 0.06 and 0.1 mol dm<sup>-3</sup> citric acid electrolytes under a high voltage of 480 and 400 V in order to consecutively grow porous alumina layers with the longest interpore distances, this followed by growth of self-organized arrays of micro-sized goblets-like niobium oxide structures and eryngii-mushrooms-like tantalum oxide structures protruding through the alumina barrier layer. The shape and size of the metal oxide microstructures were additionally tailored by post-anodizing treatment combining partial open-circuit dissolution of the alumina pores with reanodizing the underlying metal through the as grown and expanded pores. The structured metal oxide surfaces derived after selectively dissolving away the anodic alumina layers were coated with fluoroalkyl phosphate (FAP) and tested for their non-wetting properties by measuring static contact angles for water droplets. Both the FAP-coated goblet and eryngii-mushroom surfaces showed superhydrophobic behaviour with the contact angles of 158 and 156° respectively. The effect is due to the creation of composite solid–liquid–air interfaces that allow for dramatically decreased liquid-to-solid contact area and adhesion, in accord with the Cassie–Baxter model.

## **Porous Anodic Film Growth on a Zr-W Alloy**

F. Muratore, A. Baron-Wiecheć, T. Hashimoto, A. Gholinia, H. Habazaki, P. Skeldon and G.E. Thompson

*Electrochemical and Solid-State Letters*, **15**, C8-C11 (2012)

A study of the distribution of species in a porous anodic film formed on a sputtered Zr-22 atom%W alloy in a fluoride/glycerol electrolyte is presented. The film consists of nanotubes within a fluoride-enriched matrix and forms with loss of ~24% of the oxidized zirconium to the electrolyte. In contrast, loss of tungsten species is negligible, these species being retained in the nanotubes and separated from the pores by a tungsten-free region of the film material. The results suggest that the nanotubes are generated by the flow of material away from the nanotube base into the tube walls.

### **Cathodic Pulse Breakdown of Anodic Films on Aluminium in Alkaline Silicate Electrolyte – Understanding the Role of Cathodic Half-cycle in AC Plasma Electrolytic Oxidation**

S.P. Sah, E. Tsuji, Y. Aoki and H. Habazaki

*Corrosion Science*, **55**, 90-96 (2012)

Sequential anodic and cathodic pulse voltages were applied on anodised Al micro-electrodes in alkaline silicate electrolyte to explore the role of cathodic pulse in AC or bipolar plasma electrolytic oxidation (PEO) process. SEM observation was carried out to observe the sites of anodic and cathodic breakdown and their morphologies. The prior anodic breakdown accelerated the cathodic breakdown at ~50 V, and the acceleration was associated with the preferential cathodic breakdown at the anodic breakdown sites. However, the succeeding anodic breakdown during applying anodic pulse of 420 V for 2 ms was highly suppressed at the cathodic breakdown sites. This would randomise the anodic breakdown sites. Such role may contribute to the formation of rather uniform coatings on aluminium in this electrolyte without large discharge channels when larger cathodic current is applied with respect to the anodic current in AC PEO.

### **In situ X-ray Absorption Spectroscopy for Identification of Lead Species Adsorbed on a Nickel Surface in Acidic Perchlorate Solution**

M. Seo, K. Fushimi, Y. Aoki, H. Habazaki, M. Inaba, M. Yokomizo, T. Hayakawa and T. Nakayama

Journal of Electroanalytical Chemistry, **671**, 7-15 (2012)

In situ X-ray absorption spectroscopy (XAS) using a synchrotron radiation was applied to identify the Pb species adsorbed on Ni surface in acidic perchlorate solution containing  $10^{-4}$  mol dm<sup>-3</sup> Pb<sup>2+</sup> with relation to the Pb-induced stress corrosion cracking (Pb-SCC) of Ni-base alloys used as tubing materials of steam generators in nuclear power plants. The periodical emersion method under potentiostatic polarization, using the Ni plate with large specific surface area (surface roughness,  $S_r = 78.3$ ) as a working electrode, was developed to detect sensitively the sub-monolayer coverage of Pb on Ni. The Pb L<sub>III</sub> absorption spectra in a scanning XAS mode were measured by monitoring the Pb La fluorescence line. The Pb L<sub>III</sub> absorption near-edge structure (XANES) at the potential more positive than  $-0.245$  V (SHE) corresponding to the equilibrium potential of Pb-electrodeposition in  $10^{-4}$  mol dm<sup>-3</sup> Pb<sup>2+</sup> solution has revealed that the Pb species adsorbed on the Ni surface are metallic, providing the clear evidence of underpotential deposition (UPD) of Pb on the Ni surface. Moreover, the extended X-ray absorption fine structure (EXAFS) analysis was performed with a two-shell fit involving Pb–Ni and Pb–Pb interactions assuming that the Ni (1 1 1) plane is mainly exposed to the solution. The EXAFS results were convincingly explained in terms of the Pb-UPD model which represents the coexistence of the surface alloy phase and the adlayer with the same p(2x2) structure in the narrow potential range of  $-0.185$  V (SHE) to  $-0.245$  V (SHE).

### **Photo-Induced Properties of Non-annealed Anatase TiO<sub>2</sub> Mesoporous Film Prepared by Anodizing in the Hot Phosphate/glycerol Electrolyte**

Y. Taguchi, E. Tsuji, Y. Aoki and H. Habazaki

Applied Surface Science, **258**, 9810-9815 (2012)

In this study, anatase crystalline TiO<sub>2</sub> mesoporous film was formed by anodizing of titanium specimens without annealing procedures. The specimens were anodized at

3 and 20 V in  $0.6 \text{ mol dm}^{-3} \text{ K}_2\text{HPO}_4$  and  $0.2 \text{ mol dm}^{-3} \text{ K}_3\text{PO}_4$ /glycerol electrolyte at 433 K. The obtained films had mesoporous structures with pore diameters as small as  $\sim 10 \text{ nm}$ . The mesoporous film formed at 20 V without annealing (MP-20V) was a mixture of amorphous phase and nanograined anatase, which clearly showed strong  $\langle 0 0 1 \rangle$  preferred orientation, whereas that at 3 V was completely amorphous. Even without annealing, the MP-20V showed high photocatalytic activities for decomposition of water and methylene blue. In contrast, the anodic  $\text{TiO}_2$  nanotube film formed in  $\text{NH}_4\text{F}$ /ethylene glycol electrolyte revealed photocatalytic activities only after annealing at 723 K, because of the amorphous nature of the as-anodized nanotube film. The MP-20V film also showed superhydrophilicity with UV light irradiation.

### **Thickness Dependence of Proton Conductivity of Anodic $\text{ZrO}_2\text{-WO}_3\text{-SiO}_2$ Nanofilms**

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

Journal of Power Sources, **205**, 194-200 (2012)

Amorphous  $\text{ZrO}_2\text{-WO}_3\text{-SiO}_2$  nanofilms are simply prepared by anodizing of sputter-deposited  $\text{Zr}_{37}\text{W}_{47}\text{Si}_{16}$  alloy at several formation voltages for 1.8 ks in  $0.1 \text{ mol dm}^{-3}$  phosphoric acid electrolyte at  $20^\circ\text{C}$ . Efficient proton conductivity was observed after thermal treatment at  $250^\circ\text{C}$  with the conductivity enhanced by reducing the film thickness. The conductivity is enhanced more than one order of magnitude by reducing the thickness from 300 to 140 nm. The anodic oxide films consist of two layers, comprising a thin outer  $\text{ZrO}_2$  layer free from silicon and tungsten species and an inner main layer containing all zirconium, silicon and tungsten species. The thickness-dependent conductivity of the anodic  $\text{ZrO}_2\text{-WO}_3\text{-SiO}_2$  films is associated with the conductivity of the outer  $\text{ZrO}_2$  layer, which increases exponentially with reducing the film thickness. The area-specific resistivity of  $0.14 \Omega \text{ cm}^2$ , which is below the minimum requirement ( $0.2 \Omega \text{ cm}^2$ ) for a practical electrolyte membrane in commercial fuel cells, is achieved at a temperature at  $225^\circ\text{C}$  for 100 nm-thick anodic  $\text{ZrO}_2\text{-WO}_3\text{-SiO}_2$  films.

## **The Effects of Mo Addition on the Structure of Scales Formed in High Si Steel at 1150°C**

A. Zaki, M. Zainal and K. Kurokawa

Materials Science and Engineering, **576**,442-445 (2012)

High Si steels (base steel and with addition of 0.1, 0.3, 0.5mass% Mo) were oxidized in a  $N_2$ -3% $O_2$ -20% $H_2O$  atmosphere at 1150°C for 0.3-10.8ks. The oxidation kinetics showed that base steel has the highest weight gain. In contrast, 0.5Mo has the lowest weight gain. From SEM results, the scale thickness decreased as Mo content increased. Distribution of alloying elements showed that Mo is enriched in internal oxidation zone (IOZ) and played a role in slowing the outward diffusion of Fe, thus, producing a thinner Fe oxide scale and lower weight gain.

## **High Temperature Corrosion Behavior of Si-Containing Alloys in the Liquid Phase of $Na_2SO_4$ 25.7 Mass% NaCl**

T. Sudiro, T. Sano, S. Kyo, O. Ishibashi,  
M. Nakamori and K. Kurokawa

Defect and Diffusion Forum, **323-325**, 353-358 (2012)

The high temperature corrosion behavior of Si-containing alloys consisting of Cr-Si-Ni and CoNiCrAlY-Si alloys fabricated by spark plasma sintering technique was investigated in the liquid phase of  $Na_2SO_4$  + 25.7 mass% NaCl at temperatures ranging from 923-1273 K. The purpose of this study is to develop excellent corrosion resistant alloys for coating applications. Our experimental results show the CrSi<sub>2</sub> alloy with 10 mass% Ni content and the CoNiCrAlY alloy with 30 mass% Si content are the most promising materials for applications in this atmosphere. This is due to the formation of a protective SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> scale, respectively. The formation of a dense and continuous oxide layer composed and/or consisted of SiO<sub>2</sub> plays a significant role in hindering the inward diffusion of chlorine and sulfur to the alloys substrate. Particularly, the corrosion mechanism

of Cr-Si-Ni alloys and the influence of Ni addition on the corrosion resistance of CrSi<sub>2</sub> alloy are discussed in the present paper.

### **The Influence of CoNiCrAlY Addition on the High Temperature Corrosion Behavior of CrSi<sub>2</sub> Alloy in an Air-Na<sub>2</sub>SO<sub>4</sub>-NaCl Gas Atmosphere**

T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori and K. Kurokawa

Materials transactions, **53**, 1627-1632 (2012)

In this study, an attempt has been made to improve the resistance of CrSi<sub>2</sub> alloy toward high temperature corrosion and promote the formation of a continuous and slow-growing SiO<sub>2</sub> scale on the alloy surface. For this purpose, spark plasma sintering was used to fabricate the CrSi<sub>2</sub> alloys containing various amounts of CoNiCrAlY. The sintered alloys were then corroded isothermally in an air-Na<sub>2</sub>SO<sub>4</sub>-NaCl gas atmosphere at three different temperatures of 923 and 1073 K for up to 720 ks and at 1273 K for 72 ks. XRD, SEM and SEM-EDS were utilized to examine the alloy structures and compositions before and after the high temperature corrosion test. The influence of CoNiCrAlY addition on the high temperature corrosion behavior of the CrSi<sub>2</sub> alloy was clarified.

### **Tie-Line Compositions of the $\gamma$ and $\delta$ Phases in the Binary Re-Ni System**

S.Saito, T. Takashima, K. Miyama, K. Kurokawa and T. Narita

Materials Transactions, **53**, 1078-1083 (2012)

Compositions with tie lines between the  $\gamma$  and  $\delta$  phases in a binary Re-Cr-Ni system were investigated at 1423, 1573, and 1773 K by heat treating of Ar-arc-melted Re-40 at%Ni alloy. The microstructures of the Re-40 at%Ni alloy which had been water quenched after various heat treatment were observed and



their concentration profiles for Re and Ni were measured using an electron probe microanalyzer. The Re-40 at%Ni alloy consisted of the  $\gamma$  and  $\delta$  phases. The tie lined compositions of the  $\gamma$  and  $\delta$  phases are summarized as follows (in at%);  $\gamma$ : 13.4 Re-86.6 Ni,  $\delta$ : 71.7 Re-28.3 Ni at 1423 K,  $\gamma$ : 16.4 Re-83.6 Ni,  $\delta$ : 69.3 Re-30.7 Ni at 1573 K,  $\gamma$ : 20.2 Re-79.8 Ni,  $\delta$ : 65.3 Re-34.7 Ni at 1773 K. The Re-Ni alloy powder sintered using the Spark Plasma Sintering (SPS) method were investigated. Solubility limit of Ni in the  $\delta$  phase in the binary alloy system at 1423 K was found to be 28.3 at%Ni.

## **Effect of Mo Addition on High-Temperature Oxidation of Fe-Cr Alloys**

T. Syoji and K. Kurokawa

Journal of Applied Plasma Science, **20**, 39-42 (2012)

In order to clarify the effect of Mo addition on oxidation behavior of Fe-Cr alloys, high-temperature oxidation tests of Fe-18Cr-X(=0,2)Mo alloy were carried out at 1573 K in (N<sub>2</sub>-3%O<sub>2</sub>)-19.7% H<sub>2</sub>O . The addition of Mo into Fe-18Cr alloy led to the suppression of breakaway oxidation. Based on oxidation kinetics, GDS analysis, and diffusion experiment, effect of Mo on the suppression of breakaway oxidation was discussed. It was concluded that major role of Mo was in increasing diffusion coefficient of Cr in the Fe-Cr alloy.

## **Corrosion of Combustion-synthesized $\beta$ -SiAlONs in Supercritical Water**

X. Yi, A.Yamauchi, K. Kurokawa and T. Akiyama

Corrosion Science, **56**, 153-157(2012)

The corrosion of  $\beta$ -Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub>s (z = 1, 2, and 3) prepared by combustion synthesis (CS) followed by spark plasma sintering (SPS) was investigated in supercritical water at 400 °C/30 MPa for 100 h. The corrosion behavior was

studied by means of gravimetry, X-ray diffraction (XRD), scanning electron microscopy (SEM)/energy dispersive X-ray spectrometer (EDS). The mass loss and corroded layer decreased with the increasing in  $z$  value, and the results of XRD showed the oxide formed on  $\beta$ -SiAlONs ( $z = 1, 2,$  and  $3$ ) is aluminum silicate ( $\text{Al}_2\text{SiO}_5$ ). Finally, we proposed the reaction mechanism of these materials in supercritical water.

## **The Influence of Si on the Microstructure and Sintering Behavior of Ultrafine WC**

A.K. Nanda Kumar, M.Watabe and K. Kurokawa

Philosophical Magazine, **92**, 3950-3967 (2012)

The microstructure of sintered nanoscale tungsten carbide powders with 1 wt % Si addition was found to be populated by an abnormally large number of elongated grains. Interrupted sintering experiments were conducted to clarify the origins of the excessive abnormal grain growth seen in the microstructure. It was observed that rapid coarsening occurred at high temperatures owing to the formation of a liquid phase. However, the grain shape evolution during this coarsening period was found to be a consequence of excessive stacking faults and micro twins on the basal planes probably generated by reaction of WC with Si. Analyses of the microstructures and the isothermal and non isothermal coarsening behaviors suggested that the platelet morphology evolved by defect-assisted nucleation and growth on faceted grains. Based on experimental evidence from samples interrupted at low temperatures and crystal growth theories, we discuss the possible mechanisms that eventually led to the rampant platelet-type morphology. Further, the influence of such rapid grain growth on the shrinkage rate during sintering is also discussed. In comparison with the cyclic coarsening-densification process of sintering in pure nanoscale WC, the addition of Si leads to only two distinct sintering stages: either densification dominated or coarsening dominated. Concurrent densification and coarsening cannot be sustained particularly in the presence of a liquid phase that significantly enhances coarsening.

## **Maintenance of Hemiround Colonies and Undifferentiated State of Mouse Induced Pluripotent Stem Cells on Carbon Nanotube-coated Dishes**

T.Akasaka, A.Yokoyama, M.Matsuoka, T.Hashimoto and F.Watari

Carbon, **49**, 2287-2299 (2011)

Induced pluripotent stem (iPS) cells have attracted worldwide interest. However, there have been only a few studies investigating effective culture substrates for feeder-free culturing for the maintenance of iPS cells. In this study, we cultured mouse iPS cells under feeder-free conditions on carbon nanotube (CNT)-coated dishes and then evaluated the colony morphology and differentiation state of the cells on the dishes. After 5 d of cultivation in a medium containing 15% fetal bovine serum (FBS) and leukemia inhibitory factor (LIF), the colonies on thick films of multi-walled CNTs (MWCNTs) were observed to be hemiround; further, the cells expressed early undifferentiation markers. On the other hand, the colonies on a cell culture polystyrene dish and a collagen-coated polystyrene dish showed indistinct outline and spread well, and most spreading cells only weakly expressed early undifferentiation markers. These results indicate that the thick films of MWCNTs could maintain hemiround colonies and undifferentiated state of mouse iPS cells cultured under feeder-free conditions.

## **SEM Observation and Wettability of Various Processed and Fractured of Dental Zirconia**

N.Tarumi, M.Uo, E.Yamaga and F.Watari

Applied Surface Science, APSUSC-24180 (2012)

Current dental zirconia has several problems in clinical application such as chipping, fracture and detachment. To reduce these problems the surface after various treatments was analyzed by SEM observation, contact angle measurement and surface roughness measurement, and compared. The surface after mirror polishing was smooth. Porcelain layering was smooth except large formed grooves

by bubbles. After sandblast and tribochemical treatment, the surface showed several micron-sized caving with micron to submicron-level irregularities. Sandblast and tribochemical treatments with the larger roughness had the smaller water contact angle than silicone wheel polishing. Clinically fractured surface of zirconia showed a more complex structure than manually fractured surface, which may be due to the various mode of stress to be imposed repetitively to various direction.

### **Inductively Couple Investigation of Biodistribution Behavior of Platinum Particles in Mice: Correlation between d Plasma - Atomic Emission Spectroscopy and X-ray Scanning Analytical Microscopy**

S.Abe, C.Koyama, M.Mutoh, T.Akasaka, M.Uo, and F.Watari

*Applied Surface Science*, **262**, 125-128 (2012)

In this study, we investigated the biodistribution of platinum (Pt) microparticles in mice. The particles were administered through the tail vein, and then the biodistribution behavior was observed using inductively coupled plasma-atomic emission spectroscopy (ICP) and scanning X-ray analytical microscopy (XSAM). The administered particles quickly reached the spleen, liver, and lung at a constant ratio, and the ratio remained constant for four weeks. We also estimated the correlation between XSAM and ICP measurement. The relative ratio of XSAM intensity showed strong correlation with the relative ratio of Pt concentration in organs.

### **Morphology, Size Distribution and Elemental Composition of Several Dental Debris**

S.Abe, N.Iwadera, M.Esaki, K.Aoyama, T.Akasaka, M.Uo, M.Morita, Y.Yawaka, and F.Watari

*Applied Surface Science*, **262**, 245-252 (2012)

We investigated morphologies, size distributions and elemental compositions of dental debris formed by cutting/grinding teeth or dental alloys. The average size of debris formed by cutting/grinding dental alloy was around 100  $\mu\text{m}$  and that of teeth was 20  $\mu\text{m}$ . The debris formed by grinding with diamond or carborundum point had isotropic irregular shape, while the debris formed by cutting with carbide bar had characteristic lathe-cut shape. The elemental analysis indicated that the debris formed by grinding dental alloy with carborundum point consisted of not only the particles of the alloy but also the particles of Si compounds with the size of around 10  $\mu\text{m}$ . The particles of Si compounds would be formed by abrasion of the grinding instrument (carborundum, SiC). Similarly, the debris formed by grinding with diamond point also contained submicro-sized particles consisting of C compounds. The results indicate that the morphology and composition of dental debris are varied depending on the combination between the workpiece and the cutting/grinding materials and that the dental debris consist of both the workpiece and the cutting/grinding materials in some combination. In addition, some of the debris of tooth had the size less than 2  $\mu\text{m}$ , which has a potential to induce inflammation. Though the inflammation can be expected at low level, it is required to investigate the details in future.

## **Biodistribution of Water-soluble Carbon Nanotubes in Mice and its Biocompatibility**

S.Abe, S.Itoh, D.Hayashi, H.Kobayashi, T.Kiba, T.Akasaka, M.Uo, Y.Yawaka,  
S.Sato, F.Watari and T.Takada

J. Nanoscience and Nanotechnology, **12**, 700-706 (2012)

In this study, we prepared two-types of water-dispersible carbon nanotubes (CNTs) and investigated their biodistribution in mice as well as bio-/cyto-compatibility. After administration, their organs were excised at various post-injection times, then observed using both optical and transmission electron microscopy (TEM). The color of the liver and lung markedly darkened, suggesting that administered CNTs reached these organs. By TEM observation, the CNTs were found in the liver and lung. They were observed even in the kidney and spleen, though their distributions in those organs were very low compared with

that in liver and lung. Therefore, most of the administered CNTs would be accumulated in the liver or lung. However, the time profile of the body weight of CNT-administered mice was close to that of control mice. In addition, we estimated the cytocompatibility of the water-dispersible CNTs for hepatocytes. According to a TNF-alpha assay of the cells cultured with CNTs, the expression level was almost the same as that of the control. These results suggested that the water-dispersible CNTs have good bio-/cyto-compatibility under this condition.

## **A Density Functional Theory Study on Interaction of Fluorinated Ethylene Carbonate with a Graphene Surface**

S. Abe, F. Watari, and H. Tachikawa

Japanese J. Applied Physics, **51**, 10NE3401-04, (2012)

The interaction between fluorinated ethylene carbonate denoted by EC(F) and a graphene surface was investigated using of density functional theory (DFT) method. The interaction system examined was a complex composed of graphene (consisting of 14 benzene rings) and one EC(F) molecule. Ten binding sites of EC(F) binding site on the surface and edge regions of the graphene, were identified as stable points. EC(F) bound to a hexagonal position corresponding to the central of benzene ring on the graphene surface and can also bind to the edge of the graphene. The EC(F) binding energies on the surface and edge sides were 0.5 and 2.8 kcal/mol, respectively. The activation barrier for the diffusion of EC(F) on the graphene surface was significantly low (less than 0.3 kcal/mol), indicating that EC(F) can move freely on the graphene surface.

## **A Novel Approach for Direct Observation of Biodistribution of Water-soluble Carbon Nanotubes in Mice**

S.Abe, A.Hyono, F.Watari, D.Hayashi, and T.Takada

Nano Biomedicine, **4**, 143-148 (2012)

In this study, we investigated the biodistribution of water-soluble carbon nanotubes (CNTs) after administration through the tail vein of mice. The biodistribution was investigated using an optical and transmission electron measurement. Some of the CNTs remained in the liver and lung even 4 weeks post-injection. We also succeeded in direct observation of CNTs in the excited organs using Raman spectroscopy. In future, this method can allow to observation as a Raman mapping images of CNTs in body.

## **Comparison of Biodistribution and Biocompatibility of Gelatin-coated Copper Nanoparticles and Naked Copper Oxide Nanoparticles**

S.Abe, N.Iwadera, T.Narushima, Y.Uchida, M.Uo, T.Akasaka, Y.Yawaka, F.Watari, and T.Yonezawa

J. Surface Science Nanotechnology, **10**, 33-38 (2012)

In this study, we investigated the biocompatibility of gelatin-coated copper nanoparticles. To estimate their cytotoxicity, the coated copper nanoparticles were exposed to osteoblastic cells. The cell proliferation remained above 80% even when the particles concentration increased. When uncoated copper oxide nanoparticles were exposed to the cells, the proliferation ratio rapidly decreased with the concentration reaching 20% under the same conditions. To determine their biodistribution, the nanoparticles were administered to mice through their tail veins. The particles were subsequently found in some organs using an energy-dispersed X-ray spectrometer and inductively coupled plasma-atomic emission spectroscopy. The polymer-coated nanoparticles were observed in the lung, liver and spleen. They were also detected in the urine at higher concentrations than the copper oxide nanoparticles. Thus, the polymer coating is expected to improve biocompatibility by virtue of the excellent cytocompatibility and acceleration of the excretion process.

## **Morphology and Photophysical Properties of One-dimensional Arrayed Porphyrin Aggregates Assisted by Cyclodextrin Inclusion Complexation**

S.Abe, H.Kobayashi, T.Kiba, F.Watari and S.Sato

Molecular Crystals and Liquid Crystals, **536**, 151-157 (2012)

In this study, we investigated zinc-tetraphenylporphyrin/gamma-cyclodextrin complex formation based on absorption, on fluorescence and circular dichroism spectroscopy, and on fluorescence decay measurement. When the cyclodextrin concentration increased, a new absorption and fluorescence peak appeared and then circular dichroism spectra suggested a chair-like aggregate formation. These results indicated that the addition of gamma-CD enhanced J-aggregate formation. The morphology of the obtained aggregates was directly observed by SEM and TEM, which showed one-dimensional rod-like structures of 30 nm in diameter and ca. 200 nm in length.

## **Interaction of Ethylene Carbonate and Graphene Chip: Density Functional Theory Study**

S.Abe, F.Watari, and H.Tachikawa

Japanese J. Applied Physics, **51**, 01AH0701-03 (2012)

Density functional theory (DFT) calculations have been applied to complexes composed of ethylene carbonate (EC) with a graphene chip to theoretically elucidate the interaction of EC with the graphene. A graphene chip consisting of 14 benzene rings and one EC molecule were examined as the interaction system. Ten binding sites of EC were examined as binding points around the graphene chip. EC binds to a hexagonal position corresponding to the center of benzene ring of graphene surface. In addition, EC can bind to the edge region of graphene. The energy of EC in the edge region was 4.2 kcal/mol more stable than that of the hexagonal position. The activation barriers for diffusion of EC on the graphene surface were significantly low (less than 0.2 kcal/mol), indicating that EC, put on



the surface, can move freely on the graphene surface and then down into the edge region.

## **Carbonate Ion Induced Calcification using Biomimetic Enzymes with Active Reaction Center of *Carbonic Anhydrase***

S.Abe, M.Yohda, A.Nishiyama, M.Nakatani, Y.Fujii, A.Kusuhara, E.Yamatoya, T.Ishida, T.Akasaka, M.Uo, F.Watari, D.Hayashi, and T.Takada

Nano Biomedicine, **4**, 29-34 (2012)

In this study, we synthesized two types of biomimetic enzyme analogues, a macromolecules-type, and a surface modified particle type. Both of the biomimetic enzymes promoted selective hydroxyapatite formation and carbonate ion induction. Therefore, the biomimetic enzymes can be used to 1) accelerate the calcification reaction, 2) control the crystal phase, and 3) incorporate carbonate ion in hydroxyapatite. These properties can allow us to develop several carbonated hydroxyapatite materials that have potential in applications such as bone tissue engineering.

## **Conductivity Preparation by Choline Lactate Ethanol Solution for SEM Observation: Both Hard and Soft Tissues in Living Matter**

S.Abe, A.Hyono, Y.Machida, F.Watari, and T.Yonezawa

Nano Biomedicine, **4**, 18-23 (2012)

In this study, we investigated a conductivity preparation for scanning electron microscope (SEM) observation that uses a solution containing the room temperature ionic liquid (RTIL) choline lactate, which is a natural product-based tetraammonium salt. By only immersion in the choline solution, clear SEM images

of biological matter were successfully observed. In addition, we also succeeded in applying the RTIL preparation to energy-dispersed fluorescent X-ray spectroscopy (EDS) and elemental distribution mapping (SEM-EDS). This is the first time that RTIL preparation has been applied to SEM-EDS measurement instead of conventional pretreatment such as carbon sputtering. These results suggested that simple and rapid conductivity preparation using the RTIL solution can be widely applied not only SEM observation but also to SEM-EDS of a variety of living mater.

## **Interaction between Titanium and Phosphoproteins Revealed by Chromatography Column Packed with Titanium Beads**

Y.Kuboki, T.Furutake, M.Sato, Y.Sun, H.Unuma, R.Fujisawa, S.Abe, T.Akasaka, F.Watari, H.Takita, and R.Sammons

Bio-Medical Materials and Engineering, **22**, 283-288 (2012)

The biochemical mechanism behind the strong binding between titanium and living bone has not been fully elucidated, in spite of worldwide clinical application of this phenomenon. We hypothesized that one of the core mechanisms may reside in the interaction between certain proteins in the host tissues and the implanted titanium. To verify the interaction between titanium and proteins, we chose the technique of chromatography in that titanium spherical beads (45  $\mu\text{m}$ ) were packed into a column to obtain a bed volume of 16 x 50 mm, which was eluted with phosphate buffered saline (PBS) and a straight gradient system made by using PBS and 25 mM NaOH. Fetal calf serum, albumin, lysozyme, casein, phosvitin and dentin phosphoprotein (phosphophoryn) were applied to the column. Most part of albumin and lysozyme eluted with the breakthrough peak, indicating practically no affinity to titanium. Fetal bovine serum also eluted mostly as the breakthrough peak, but distinct retained peak was observed. On the other hand, alpha-casein, phosvitin and phosphophoryn exhibited a distinct retained peak separated from the breakthrough peak. We proposed that phosphate groups (phosphoserines) in the major phosphoproteins, alpha-casein, phosvitin and phosphophoryn may be involved in the binding of these proteins with titanium.

## **Chemical Immobilization of Multi-walled Carbon Nanotubes onto Glass Surface in Aqueous Media**

T.Takada, Y.Konno, K.Nakayama, P.T.Dunuwila, Y.Maeda, and S.Abe

Nano Biomedicine, **4**, 113-117 (2012)

Amide bond formation between carboxylated multi-walled carbon nanotubes (MWCNT-COOHs) and a glass surface with a water-soluble condensing agent in aqueous media was examined to make a transparent conductive material. The condensing agent used was DMT-MM (4-(4,6-dimethoxy-1, 3, 5-triazin-2-yl)-4-methylmorpholinium chloride). The extent of immobilization depended on the DMT-MM content in solution; and an optimum concentration of DMT-MM was found to exist. Finally, a mechanism for the variation of the extent of immobilization as a function of DMT-MM content was proposed.

## **Density Functional Theory (DFT) Study on the Addition of Hydroxyl Radical (OH) to C<sub>20</sub>**

T.Iyama, S.Abe and H.Tachikawa

Molecular Crystals and Liquid Crystals, **567**, 200-206 (2012)

The radical addition to the smallest fullerene C<sub>20</sub> has been investigated by means of density functional theory (DFT) method in order to elucidate the radical scavenge mechanism of fullerene. The OH radical was examined as an organic radical because the radical has a high reactivity. The DFT calculation showed that the OH radical binds directly to the carbon atom of C<sub>20</sub> and a strong C-O bond is formed. The binding energies of the first addition of OH radical were calculated to be 85.2 kcal/mol at the B3LYP/6-311G(d,p) level of theory. In the second radical addition, the binding energy of OH to C<sub>20</sub> (OH) was 91.5 kcal/mol. The unpaired electron was distributed widely over the C<sub>20</sub> surface in the C<sub>20</sub> (OH) complex.

## **Spectral Narrowing of UV-visible Absorption and Emission Spectra of Anthracene-derivatives in $\beta$ -cyclodextrin Nanocavity: Effects of Host/guest Stoichiometry**

S.Sato, Y.Yoshizumi, T.Kiba, A.Murayama, and S.Abe

Molecular Crystals and Liquid Crystals, **568**, 60-66 (2012)

Cyclodextrins (CD) are cyclic oligosaccharides consisting of six or more D-glucopyranose units, the interior of which forms a hydrophobic cavity. In the present study, we employed the CD confinement effects as a tool to suppress an electronic decoherence of guest wavefunction by reducing intermolecular interactions between a guest molecule and the surrounding environment. Effects of host/guest stoichiometry on the decoherence suppression were investigated by comparing native beta-CD with trimethyl-beta-CD that should form only a 1: 1 complex. Both fluorescence and fluorescence-excitation spectra of inclusion complexes exhibited spectral narrowings only for the beta-CD host, suggesting that the formation of barrel-type beta-CD dimer plays a key role for the pronounced spectral narrowings.

## **Amide Bond Formation between Carboxylated Multi-Walled Carbon Nanotubes and Glass Surface by Using Carbodiimide Condensing Agent and Triazole Derivatives**

K.Nakayama, T.Takada, S.Abe, Y.Honda, H.Ikeyama, Y.Nakaya and A.Furusaki

Molecular Crystals and Liquid Crystals, **568**, 38-45 (2012)

Amide bond formation between carboxylated multi-walled carbon nanotubes (MWCNT-COOHs) and aminated glass surface has been studied to make transparent conductive device. Examining the condensation reaction between MWCNT-COOHs and glass surface under various conditions, it has been found that MWCNT-COOHs are immobilized on the surface by reaction using a

carbodiimide and a triazole. The MWCNT layers formed are not easily detached; the interaction between MWCNTs and glass surface is quite strong, implying formation of chemical bonding. Immobilization of MWCNTs on the surface is confirmed also by scanning electron microscopy. Electric conductivity of MWCNT-coated glass has been preliminarily measured.

## **Effects of Fluid Directions on Heat Exchange in Thermoelectric Generators**

Ryosuke O. Suzuki, Yuto Sasaki, Takeyuki Fujisaka and Min Chen

J. Electron. Mater., 41 (6) 1766-1770 (2012)

Thermal fluids can carry heat to the large surface of a thermoelectric (TE) panel from hot and/or cold sources. The TE power thus obtainable was precisely evaluated using numerical calculations based on fluid dynamics and heat transfer. The commercial software FLUENT was coupled with a TE model for this purpose. The fluid velocity distribution and the temperature profiles in the fluids and TE modules were calculated in two-dimensional space. The electromotive force was then evaluated for counter-flow and split-flow models to show the effect of a stagnation point. Friction along the fluid surface along a long, flat path was larger than that along a short path split into two parts. The power required to circulate the fluids along the flow path is not negligible and should be considered in TE generation system design. [dx.doi.org/10.1007/s11664-012-2074-x](https://doi.org/10.1007/s11664-012-2074-x)

## **CO<sub>2</sub> Decomposition Using Electrochemical Process in Molten Salts**

Koya Ohtake, Hiroshi Kinoshita, Tatsuya Kikuchi, Ryosuke O. Suzuki

J. Physics: Conference Series, 379 (1) 012038 (2012)

The electrochemical decomposition of  $\text{CO}_2$  gas to carbon and oxygen gas was studied in  $\text{LiCl-Li}_2\text{O}$  and  $\text{CaCl}_2\text{-CaO}$  molten salts. This process consists of electrochemical reduction of  $\text{Li}_2\text{O}$  and  $\text{CaO}$ , as well as the thermal reduction of  $\text{CO}_2$  gas by the respective metallic  $\text{Li}$  and  $\text{Ca}$ . Two kinds of  $\text{ZrO}_2$  solid electrolytes were tested as an oxygen ion conductor, and the electrolytes removed oxygen ions from the molten salts to the outside of the reactor. After electrolysis in both salts, the aggregations of nanometer-scale amorphous carbon and rod-like graphite crystals were observed by transmission electron microscopy. When 9.7 % $\text{CO}_2\text{-Ar}$  mixed gas was blown into  $\text{LiCl-Li}_2\text{O}$  and  $\text{CaCl}_2\text{-CaO}$  molten salts, the current efficiency was evaluated to be 89.7 % and 78.5 %, respectively, by the exhaust gas analysis and the supplied charge. When a solid electrolyte with higher ionic conductivity was used, the current and carbon production became larger. It was found that the rate determining step is the diffusion of oxygen ions into the  $\text{ZrO}_2$  solid electrolyte. [doi:10.1088/1742-6596/379/1/012038](https://doi.org/10.1088/1742-6596/379/1/012038)

## Reduction of Titanium Oxides in Molten $\text{CaO-CaCl}_2$

Naoto Kobayashi, Kei-ichi Kobayashi, Tatsuya Kikuchi and Ryosuke O. Suzuki

Proc. 12th World Conf. on Titanium, June 19-24, 2011, China National Convention Center, Beijing, China, ed by Lian Zhou, Hui Chang, Yafeng Lu and Dongsheng Xu, Science Press, Beijing, China, (2011) vol.I, pp.84-86.

OS process to reduce  $\text{TiO}_2$  was studied. At the initial stage of  $\text{TiO}_2$  reduction,  $\text{CaTiO}_3$  is formed by thermochemical reaction between  $\text{TiO}_2$  and  $\text{CaO}$  and delays reduction. At the later stage, the volume of particle grows up 10,000 times larger than that of  $\text{TiO}_2$ , and the slow oxygen diffusion in a long distance delays the deoxidation. In the case of reduction of  $\text{CaTiO}_3$ , current efficiency was very high at the initial stage, and became low at the later stage, because  $\alpha\text{-Ti}$  was formed. In case of reduction of  $\text{TiO}$ , dense  $\text{Ti}$  layer covered the surface of  $\text{TiO}$  and it blocked inward diffusion of  $\text{Ca}$  and the outward diffusion of oxygen. The thick  $\text{Ti}$  layer on the unreacted particles delays the deoxidation and its rate depends on oxygen diffusion in this layer.

## **Electrolysis of CaO in the Molten CaCl<sub>2</sub> for Direct Reduction of TiO<sub>2</sub>**

Ryosuke O. Suzuki, Naoto Kobayashi, Kei-ichi Kobayashi, Daisuke Yamada, Shogo Osaki, Reyna Famila Descaller-Arriescado, and Tatsuya Kikuchi

Proc. 12th World Conf. on Titanium, June 19-24, 2011, China National Convention Center, Beijing, China, ed by Lian Zhou, Hui Chang, Yafeng Lu and Dongsheng Xu, Science Press, Beijing, China, (2011) vol.I, pp.84-86.

Electrochemical behavior of CaO-CaCl<sub>2</sub> melt was studied from several experimental approaches to promote “OS process”, i.e., the calciothermic reduction of the titanium oxide with electrolysis of CaO dissolved in the molten CaCl<sub>2</sub>. The predicted existence of Ca concentrated region near the cathode was experimentally confirmed both by the reduction under electrical isolation and by wet chemical analysis of the solidified salts. It is deduced from the electrode-shielding methods that the total rate of CaO electrolysis is controlled by O<sup>2-</sup> transportation in the CaCl<sub>2</sub>-CaO melt. In CaTiO<sub>3</sub> reduction, however, the oxygen diffusion in the formed Ti layer and the anodic surface area is rate-determining factors. The oxygen absorbing anode based on LaGaO<sub>3</sub> ionic conductor could carry up the oxygen gas from the CaCl<sub>2</sub> melt.

## **Decomposition of CO<sub>2</sub> Gas in CaCl<sub>2</sub>-CaO and LiCl-Li<sub>2</sub>O Molten Salts**

Ryosuke O. Suzuki, Koya Ohtake, Tetsuya Uchiyama, Hiroshi Kinoshita, Norihito Sakaguchi, Tatsuya Kikuchi

ECS Transactions, 50 (11) 443-450 (2012)

The electrochemical decomposition of CO<sub>2</sub> gas to form carbon and oxygen gas was studied in CaCl<sub>2</sub>-CaO and LiCl-Li<sub>2</sub>O molten salts. A constant voltage was applied at 1173K and 923K, respectively. This process consists of (1)electrochemical

reduction of oxide (formation of reductant), (2) thermal reduction of  $\text{CO}_2$  gas by reaction with the metal dissolved in the molten salt, and (3)  $\text{ZrO}_2$  anodic electrode worked as an oxygen ions conductor to remove oxygen ions from the molten salt. When 9.7 %  $\text{CO}_2$ -Ar mixed gas was blown into  $\text{CaCl}_2$ -CaO and  $\text{LiCl}$ - $\text{Li}_2\text{O}$  molten salts, the current efficiency was evaluated to be 78.5 % and 89.7 %, respectively, judged by the exhaust gas analysis and the supplied charge. After electrolysis, the aggregations of carbon nano-tubes (CNT) and amorphous carbon particles were often observed by transmission electron microscope. [doi:/10.1149/05011.0443ecst](https://doi.org/10.1149/05011.0443ecst)

## **Reduction of Niobium Oxide Using $\text{CaCl}_2$ Melt**

Ryosuke O. Suzuki, Isamu Ueda, Tatsuya Sato, Masahiko Baba and Tatsuya Kikuchi

Proc. 4th Asian Conference on Molten Salt Chemistry and Technology, Sept.23-27, 2012, Hotel Taikanso, Matsushima, Japan, Molten Salt Committee, the Electrochemical Society of Japan. pp.29-35. (2012)

Niobium oxide powder was reduced in the molten  $\text{CaCl}_2$ . During the electrolysis of CaO in the melt, calcium deposited is used as the reductant and the by-product CaO is removed by dissolution into  $\text{CaCl}_2$  melt. Oxygen is extracted at the graphite anode as  $\text{CO}/\text{CO}_2$  gas evolution. The morphology of the samples was examined and the pulverization mechanism was proposed based on the formation of  $\text{CaNb}_2\text{O}_6$ . The pulverization was studied via calciothermic reduction of  $\text{Nb}_2\text{O}_5$  and NbO without electrolysis and the morphology is compared with that by the electrolysis.

## **Optimization of Design in Cascade-Type Thermoelectric Module**

Ryosuke O. Suzuki and Takeyuki Fujisaka

Proc. Powder Metallurgy World Congress and Exhibition (PM2012 YOKOHAMA), Sept.23-27, 2012, Pacifico Yokohama, Yokohama, Japan, the



Japan Society of Powder and Powder Metallurgy (JSPM), (2012) 16E-S1-17, "0463\_201211060004.pdf" in CDROM (ISBN:978-4-9900214-9-8).

Cascade-type structure is effective to adjust the thermal properties of the thermoelectric (TE) elements to the working temperature of module, because the material performance ( $Z$ ) depends on the temperature. Conventionally the same number of TE pairs has been joined to form the two or three layers. Because the heat flux penetrates these layers from the hot to the cold terminals, the junction temperatures of these layers are determined by the thermal properties of TE elements and material size. This study optimizes the material size and the number of pairs considering the material properties. One-dimensional analytical solution can estimate the power from the cascade module. For example, three layer structure consisting of the six materials ( $ZT < 1$  for all) can give the thermal efficiency as high as 19% between 1200 and 300 K. It is essential to select the best materials with a low thermal conductivity but also important to design the best dimension.

## **Dimensional Optimization of Thermoelectric Modules for Solar Power Generation**

Takeyuki Fujisaka and Ryosuke O. Suzuki

Proc. IECON 2012 - 38th Annual Conference on IEEE Industrial Electronics Society. 25-28 Oct., 2012, Ecole de Technologie Superieure de Montreal, Universite du Quebec, Montreal, Canada, The Institute of Electrical and Electronics Engineers (IEEE), NJ 08854 USA, (2012) 5868-72.

A thermoelectric generation system is examined based on heat transfer analysis when solar heat is taken as the heat source. Under a constant heat flux condition from a solar collector, external load and leg length were numerically optimized to obtain maximum power. A special functions are imbedded in the commercial software FLUENT. The optimal external load is different from the traditional condition that the external and internal loads are equal. The optimal leg length was derived analytically by using a reasonable set of assumptions. [doi:10.1109/IECON.2012.6389124](https://doi.org/10.1109/IECON.2012.6389124)

## Power Generation Using the Fluids Blown Perpendicular to the TE Panel

Ryosuke O. Suzuki, Yuto Sasaki, Takeyuki Fujisaka and Min Chen

Proc. IECON 2012 - 38th Annual Conference on IEEE Industrial Electronics Society. 25-28 Oct., 2012, Ecole de Technologie Superieure de Montreal, Universite du Quebec, Montreal, Canada, The Institute of Electrical and Electronics Engineers (IEEE), NJ 08854 USA, (2012) 5873-78.

Temperature difference is given to thermoelectric (TE) flat panel using two thermal fluids. The TE power is mathematically evaluated when a fluid is perpendicularly blown onto the center of the TE panel and when it divided to two opposite directions at the equivalent mass flow rate. The non-dimensional analysis using analytical solutions shows that the output power becomes completely identical with that for the non-split flow along the single flat TE panel. The fluid velocity distribution and the temperature profiles were numerically calculated using the finite volume method to show the effect of stagnation and friction in the long flat path. [doi:/10.1109/IECON.2012.6389123](https://doi.org/10.1109/IECON.2012.6389123)

## Thermoelectric Properties of n-Type $\text{Mn}_{3-x}\text{Cr}_x\text{Si}_4\text{Al}_2$ in Air

R. Funahashi, Y. Matsumura, H. Tanaka, T. Takeuchi, W. Norimatsu, E. Combe,  
R. O. Suzuki, Y. Wang,  
C. Wan, S. Katsuyama, M. Kusunoki, K. Koumoto,

J. Applied Phys. 112, (7) 073713 (2012)

A silicide material with a good n-type thermoelectric property has been found. This silicide possesses a composition of  $\text{Mn}_{3-x}\text{Cr}_x\text{Si}_4\text{Al}_2$  ( $0 \leq x \leq 0.7$ ) and hexagonal  $\text{CrSi}_2$  structure. The  $a$ - and  $c$ -cell parameters decreased with increasing the amount of Cr substitution. The absolute values of Seebeck coefficient and

electrical resistivity increased by Cr substitution up to 573 K because of reduction of carrier density. The dimensionless thermoelectric figure of merit  $ZT$  reached 0.21 at 773 K for a non Cr substituted sample at the Mn site and 0.30 at 573 K for a Cr substituted one with  $x = 0.3$ . Since oxide passive layer was formed around the surface, electrical resistivity measured at 873 K was constant for 2 days in air, which indicates good oxidation resistance in air of this material. The  $Mn_{3-x}Cr_xSi_4Al_2$  is a promising n-type material with a good oxidation resistance in the middle temperature range. A thermoelectric module consisting of 64 pairs of legs was fabricated using  $MnSi_{1.7}$  and non Cr substituted  $Mn_3Si_4Al_2$  devices as p- and n-type legs, respectively. Output power reaches 9.4 W, which corresponds to  $2.3 \text{ kW/m}^2$  of power density against surface area of the substrate, for a heat source temperature of 873 K in air. [doi:/10.1063/1.4755793](https://doi.org/10.1063/1.4755793)

## **DFT Study of 2-butyne-1,4-diol Adsorption on Ni(111) or Ni(100) Clusters**

T. Sakamoto, H. Tachikawa, K. Azumi

*Applied Surface Science*, **258**, 6785-6792 (2012)

Density functional theory (DFT) calculation was applied to acetylene (AC) and 2-butyne-1,4-diol (BD) adsorbed on an Ni(1 1 1) or Ni(1 0 0) model cluster surface in order to elucidate the relationship between their electronic states and geometry in the adsorption process. Adsorption energy of AC calculated using BSSE correction and binding structure were in good agreement with the experimental data. The geometry and adsorption energy of AC or BD on the Ni(1 1 1) surface in the optimized adsorption condition differ from those on the Ni(1 0 0) surface. Analysis of a natural electron configuration of adsorbates before and after adsorption on Ni clusters clarified that the 2s orbital rather than other orbitals such as 2p contributed mainly to the adsorption energy.

## **Improvement of Al Coating Adhesive Strength on the AZ91D Magnesium Alloy Electrodeposited from Ionic Liquid**

J. Tang, K. Azumi

*Surface and Coatings Technology*, **208**, 1-6 (2012)

Adhesive strength of Al coatings electrodeposited on AZ91D in aluminum chloride / 1-ethyl-3-methylimidazolium chloride was improved by the development of a zincate pretreatment and optimized current pulse electrodeposition method. A dense Zn layer was deposited on both the  $\alpha$ - and  $\beta$ -phase surfaces of AZ91D substrate pre-treated in a  $\text{Cu}^{2+}$  added activation bath prior to the zincate process. On this zincated substrate an Al coating was electrodeposited by bipolar current pulse polarization and the adhesive strength of the Al coating to the substrate was better than 11 MPa. The Al coating obtained under the optimal condition also showed good corrosion resistance in 3.5 wt.% NaCl solutions.

## **Effects of Minor Elements in Al alloy on Zincate Pretreatment**

S. Egoshi, K. Azumi, H. Konno, K. Ebihara, Y. Taguchi

*Applied Surface Science*, **261**, 567-573 (2012)

The effects of minor elements in Al alloys on Zn deposition during double zincate pretreatment were investigated using four Al alloys: Al foil containing ca. 55 ppm Cu (Al(Cu)), Al-1%Si (Al(Si)), 99.99% Al (Al(4N)) and 99.999% Al (Al(5N)). SEM images showed that a uniform Zn layer was deposited on Al(Cu) and Al(Si) but not on Al(4N) or Al(5N) after the double zincate process. Immersion potential during the zincate process indicated that the duration of substitution reaction of Zn deposition and Al dissolution on Al(Cu) was shorter than that on the other alloys. These results suggest that a small amount of Cu increases the efficiency of the zincate process and the density of Zn deposition. Etching pretreatment of alloys in sulfuric acid containing  $\text{Cu}^{2+}$  ions before zincate pretreatment dramatically improved the uniformity and efficiency of Zn deposition on Al(Si) but not on Al(4N) or Al(5N), indicating that small and dispersed Cu particles were deposited efficiently on the Al(Si) alloy and provided Zn nucleation sites. From the results, it was concluded that the activity level of native Al for the zincate process is

considerable low and is thus dramatically affected by alloying or surface modification with a small amount of electrochemically active elements.

## **Micro-fabrication of Titanium Surface Using Flowing-type Micro-Droplet-Cell**

K. Fushimi, H. Watanabe, T. Nakanishi, Y. Hasegawa

*J. Surf. Finish. Soc. Jpn* **63**(6), 375-380 (2012). In Japanese

Flowing-type micro-droplet-cell (f-MDC) was applied to the anodic polarization of titanium surface in sodium chloride containing ethylene glycol solution. Anodic current due to removing surface oxide and dissolving substrate was flowed locally at the area limited with f-MDC and formed a hole on the surface. The shape and morphology of the hole formed was dependent on applied voltage, polarization time, flowing volume rate as well as capillary employed for the f-MDC. The suitable condition for the polarization with f-MDC was discussed in order to obtain an ordered hole.

## **Effects of Thickness and Field Strength of Anodic Oxide Film on Aluminum on its Compressive Rupture**

T. Yamamoto, K. Fushimi, A. W. Hassel, H. Konno

*Corros. Rev.* **30**(5-6), 199-207 (2012)

The rupture behavior of an anodized aluminum surface was investigated in a borate buffer solution using an *in situ* micro-indentation test, in which transients of the indentation load and flowing current were monitored during loading and unloading of a sapphire indenter. A pair of anodic current peaks emerged during both downward and upward drives of the indenter due to rupture and repair of an anodic oxide film. The total area of film ruptured during both drives, as well as the area of radial cracks, increased with an increase in film thickness and with a decrease in electric field applied while an area of circular cracks was almost constant. It was suggested that the film-rupture owing to radial cracks formation

was enhanced by tensile stress accumulated in the anodic oxide film by thickening of the oxide film and lowering of the electrostriction.

## **Influence of Desiccation Procedures on the Surface Wettability and Corrosion Resistance of Porous Aluminium Anodic Oxide Films**

M. Zheng, M. Sakairi , H. Jha

Corrosion Science, **55**, 332-338 (2012)

A hydrophobic oxide film was formed on aluminium by anodizing followed by desiccation treatment. Films subjected to gradual heating and cooling exhibit larger water contact angles than samples exposed to fast heating and cooling at the same temperature. From SEM and Auger Electron Spectroscopic observations, the low wettability surface shows a regular porous morphology with no significant chemical composition differences due to the different treatments. The desiccation process improves the corrosion resistance, shown by immersion in NaCl. The change in morphology by the desiccation processes is considered a main reason to lower the wettability, which further affects the corrosion properties.

## **Structure Control of Cu-Zn Microchannel Lining Layers with Electrochemical Dissolution**

K. Kobayashi, T. Ohmi, T. Kumagai, M. Sakairi and M. Iguchi

J. JSEM Special Issue, **12**, s213-216 (2012)

The effect of potentiostatic dissolution on the structure of a Cu-Zn alloy microchannel lining layer was investigated. The microchannel lining layer was fabricated by a powder-metallurgical process using copper powder and zinc wire. The lining layer became more porous after potentiostatic dissolution at a constant potential of  $-0.5$  V vs. Ag/AgCl. The lining layer was remarkably dezinced and it contained many open pores under the dissolution condition at  $+0.5$  V. These results indicate the possibility of precise structure control of the microchannel lining layer.

## **Anodic Oxidation Behavior of Al-Zn Alloy Lining Layer Produced by a Sacrificial-Core Method**

M. Ishida, T. Ohmi, M. Sakairi, M. Iguchi

J. JSEM Special Issue, **12**, s222-s225 (2012)

We investigated the influence of Zn on anodic oxidation of planner Al-Zn lining layers produced by a sacrificial-core method. The Al-Zn lining layer was produced from aluminum powder and zinc plate. By comparison with experiments using sintered aluminum powder compacts, it was found that zinc hindered the formation of nanoporous alumina film. The nanoporous structure can be formed on the surface of the Al-Zn alloy lining layer by long time anodic oxidation of 7.2 ks.

## **Composition and Structure Changes in Al<sub>3</sub>Ni<sub>2</sub> Microchannel Lining Layers by Alkali Leaching**

Y. Saito, T. Ohmi, M. Sakairi, T. Kumagai and M. Iguchi

J. JSEM Special Issue, **12**, s237-242 (2012)

Effects of alkali leaching time on the composition and structure changes in the Al Ni microchannel lining layer produced by a sacrificial-core method have been investigated. The composition was measured both on the specimen surface directly exposed to the leachant and on the new surface cut after alkali leaching. In each surface, the decrease in Al concentration became sluggish after formation of Ni Al. On the other hand, nano structure consisted of almost pure Ni was detected on the inner wall of the microchannel leached for 864 ks.

## **Corrosion Resistance and Passive Film Characterization of 9Cr Oxide Dispersion Strengthened Steel in Acidic and Chloride Environment**

S. Ningshena, M. Sakairi K. Suzuki and S. Ukai

Proc of 6th Japan-China Joint Seminar on Marine Corrosion, **No. 02** (2012)

The most important issue for the application of ODS steel is to understand their corrosion resistance behaviour in different environment. In the present work, corrosion resistance and passive film characteristic of 9 % Cr Oxide Dispersion Strengthened (ODS) ferritic steel in different acidic (0.5 M H<sub>2</sub>SO<sub>4</sub> with or without chloride, 1 - 6 M HNO<sub>3</sub>) and chloride media (0.1 - 0.5M NaCl) were evaluated. The results of the open circuit potential show nobler potential value for measurements in borate and nitric acid media and more active value in 0.5M NaCl solution. The potentiodynamic polarization plots and its measured parameters indicated clear influences of different electrolytes on the corrosion resistance of this investigated alloy. Higher transpassive potential was observed for measurements in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1- 6 M HNO<sub>3</sub> media but shift in corrosion potential was observed with increase in concentration from 1 M HNO<sub>3</sub> to 6 M HNO<sub>3</sub>. However, in acidic-chloride and chloride media (0.1M NaCl and 0.5 M NaCl) low pitting potential and high anodic dissolution was observed. The X-ray Photoelectron Spectroscopy (XPS) analyses of the pre-passivated and after polarization surface indicated that the oxides are mostly composed of Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> along with Y<sub>2</sub>O<sub>3</sub> and very little of Ti, W and Ni elements. The SEM morphology of pits revealed globular feature for the pitted sample and the oxidized oxide layer appears mostly uniform.

## **Porous Structure Control of Hydrophobic Aluminum Oxide Film and Its Corrosion Protection Study**

M. Zheng, M. Sakairi and H. Jha

Proc of 6th Japan-China Joint Seminar on Marine Corrosion, **No. 39** (2012)

Research in hydrophobic surface on aluminium has aroused much attention recently, according to its potential of wide practical application, and hydrophobic films have been successfully fabricated by various methods. However, almost every technique makes use of organic coating as the final step, which leads to



some problem such as environmental pollution, unendurable or energy consuming. In previous studies, it is found desiccation in oven is an effective treatment to lower the wettability of PAOF (Porous Anodic Oxide Film), and by controlling the temperature rising rate and desiccation time, samples with different wettability can be obtained. In this study, the wettability of aluminium samples anodized for different time is mainly discussed.

From the cross section of samples, the thickness of PAOF grows at a rate of 4.2 nm/s as anodizing time expanding in phosphoric acid. The sample anodized for 7.2 ks shows a higher increasing rate of Water Contact Angle (CA) than sample anodized for 1.8 ks and 3.6 ks, possibly because its better regularity of porous layer. However, after a longer desiccation time, the air pressure change in micropores seems not to have an evident influence on the CA. In polarization curves, it is found that hydrophobic samples have better corrosion resistance than anodized sample. After sufficient desiccation, the sample anodized for 3.6 ks has the similar corrosion resistance to the sample anodized for 7.2 ks. Based on the interface model, the CA and corrosion resistance of hydrophobic PAOF could be explained.

## **Formation of Alumina Films with Nano-dots Structures by Liquid Phase Deposition and Anodizing**

M. Sakairi, R. Fujita, H. Jha and T. Kikuchi

Proc. of ASST2012, No. 53 (2012)

A combination process of liquid phase deposition (LPD) treatment and anodizing were employed to form alumina film with nano-dots structures. During LPD treatments, localized dissolution could be occurred under the pre-anodized film to form pits. As re-anodizing, these pits were filled with anodic aluminum oxide to form nano-dot structure. Modification of LPD time and temperature are make it possible to form alumina nano-dots structures, which size are lower than 1  $\mu\text{m}$ . Because the pits size under the pre-anodized oxide film is increasing with LPD treatment time, closed nano-dots are formed.

## **Analysis of Surface Film and Morphology of 3003 Aluminum Alloy After Immersion in Different Cation Contained Model Tap Waters**

M. Sakairi, K. Otani, A. Kaneko, Y. Seki and D. Nagasawa

Proc. of ASST2012, **No.83** (2012)

The effect of metal cations,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ , on oxide film structure and morphology change during immersion corrosion tests of 3003 aluminum alloy in model tap waters is investigated by surface analysis techniques such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy. The hardness of metal cation based on hard and soft acids and bases, HSAB, is applied to explain the effect of its on passive oxide film structure. It was found that there is a lot of nano-sized pits were observed after 86.4 ks immersed in metal cation containing model tap water, and nano-sized corrosion products were also observed especially specimen immersed in  $\text{K}^+$  solutions. According to AES and XPS results, hard metal cations like  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  was existed in surface oxide film, while soft metal cations were not existed in the oxide films.

## **Evaluation of Cations Effect on Corrosion of Al in Model Tap Water by HSAB Theory**

M. Sakairi, K. Otani, A. Kaneko, Y. Seki and D. Nagasawa

Proc. of Eurocorr2012, **No. 1390**, (6 pages) (2012)

The effect of metal cation on corrosion of aluminium in model tap water was examined by galvanic corrosion tests. A hardness of metal cation, which was based on hard acid and soft base concept, was employed to explain the effect of metal cation. Both potential and current fluctuations, that were related to each event of localized corrosion, were observed. The potential and current fluctuation correlated with each other. The charge during galvanic tests decreases whit increasing hardness of metal cations, and this results may explain by hard metal cation

incorporated in the passive films to strengthen the passive films and to increase anticorrosive property of the passive films.

### **Effect of Acetate Ions on Polarization Behavior of Low C-13%Cr Stainless Steel in Acid NaCl Solutions**

M. Sakairi, J. Tatehara, A. Kikawa and S. Hashizume  
Proc. of The 16th APCCC, 0103\_F (2012)

The influence of acetate ions on corrosion behavior of stainless steels in oil and gas environments is not clear. The effect of acetate ions on corrosion behavior of low carbon 13% Cr stainless steel was examined in 20 mass% NaCl with 0 to 4 g/L CH<sub>3</sub>COONa (pH=4.5 and 7) by electrochemically. No significant effect of acetate ions addition was observed on pitting potential, while rest potential slightly changed with acetate ions addition at pH=4.5 with deaerated solutions. A pseudo-passive region, however, was observed except for solution of pH = 4.5 and no addition of CH<sub>3</sub>COONa without N<sub>2</sub> gas bubbling. In solutions with deaerated at high temperature, the current at the region decreased with increasing concentration of acetate ions. The results suggested that acetate ions change the protectiveness of the passive film formed on the steel.

### **Alkali Leaching of Cu-Al Alloy Microchannel Lining Layer**

A. Maruyama, T. Ohomi, M. Sakairi and M. Iguchi

Proc. of ISEM-ACEM-SEM-7th ISEM'12-Taipei, O108 (2012)

In order to produce a Raney copper catalyst on the inner wall of microchannels, alkali leaching of Cu-Al alloy microchannel lining-layers was investigated. Aluminum concentration of the lining layer decreased with leaching time when the lining-layer surface was exposed to a leaching solution. Furthermore, a fine copper structure was formed where the aluminum was leached. This result indicates a possibility of fabrication of Raney copper catalyst.

## **Formation of Nanoporous Structures on Al-Zn Alloy Lining Layers by Anodic Oxidation**

M. Ishida, T. Ohmi, M. Sakairi and M. Iguchi,

Proc. of ISEM-ACEM-SEM-7th ISEM'12-Taipei, O109 (2012)

We investigated the anodic oxidation of planner Al-Zn lining layer to produce a nanoporous oxide film. The Al- Zn lining layer was produced by a sacrificial-core method using aluminum powder and zinc plate. No nanoporous structure was observed in the specimen after anodic oxidation at 50 V and 100 V for 7.2 ks. In the case of longer anodic oxidation time, 14.4 ks, the nanoporous oxide film was formed on a part of the specimen at the same voltages. Furthermore, it was formed in the entire region in the case of 150 V for 7.2 ks or longer.

## **In Situ X-ray Diffraction of Surface Oxide on Type 430 Stainless Steel in Breakaway Condition Using Synchrotron Radiation**

I. Saeki, Y. Sugiyama, S. Hayashi, A. Yamauchi, T. Doi, Y. Nishiyama, S. Kyo, S. Suzuki, M. Sato, and S. Fujimoto

Corrosion Science, **55**, 219-225 (2012)

Changes in the crystal structure of type 430 stainless steel and the oxides on its surface were studied in situ at 1373 K using a high-intensity synchrotron X-ray source provided by SPring-8 in Japan. The surface of the steel was initially covered with  $\text{Cr}_2\text{O}_3$ , which was then converted to  $\text{FeCr}_2\text{O}_4$ , and finally  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  formed on it. These results indicated that the reason for the breakaway oxidation in type 430 stainless steel is Cr depletion beneath  $\text{Cr}_2\text{O}_3$  layer and the subsequent ionisation of Fe, not the simple mechanical failure of  $\text{Cr}_2\text{O}_3$ .

## **Phase Transformation Behavior of Al<sub>2</sub>O<sub>3</sub> Scale Formed on Pt-Modified $\gamma'$ -Ni<sub>3</sub>Al-Based Alloys With and Without Hf Addition**

S. Hayashi, B. Gleeson

Oxidation of Metals, **77**, 237-251 (2012)

The allotropic phase transformation behavior of Al<sub>2</sub>O<sub>3</sub> scale formed on Ni-22Al-30Pt (in at.%) with and without 0.5Hf was investigated during short-term (i.e., 3 min dwell) cyclic oxidation at 1,150 °C in air. Hafnium addition did not appear to affect the oxidation rate in the early oxidation cycles, but it did delay the phase transformation from the metastable  $\theta$ -Al<sub>2</sub>O<sub>3</sub> structure to the stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Small dimples, which corresponded to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> grains, started to form on the Hf-free alloy after only three oxidation cycles; whereas, no apparent morphological change of the oxide scale surface was observed on the Hf-modified alloy. The transformation to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was found to initiate at scale/alloy interface on the Hf-free alloy, but it initiated at gas/scale interface on the Hf-modified alloy. Depth profiling using glow discharge optical emission spectroscopy revealed that Hf enriched at the scale/alloy interface due to Hf rejection associated with the formation of an Al-depleted c-layer, which has a low Hf solubility. Higher positive strain energy due to Hf solution in the metastable Al<sub>2</sub>O<sub>3</sub> was inferred to be the main contributor to the delayed transformation.

## **Formation of Exclusive Al<sub>2</sub>O<sub>3</sub> Scale on Nb and Nb-rich Alloys by Two-Step Oxygen-Aluminum Diffusion Process**

S. Hayashi, S. Takagi, R. Yamagata, T. Narita, and S. Ukai

Oxidation of Metals, **78**, 167-178 (2012)

External Al<sub>2</sub>O<sub>3</sub> scale formation behavior by a diffusion aluminizing process on Nb and Nb-X (X = Mo, Re, and Ta) alloys with different oxygen solubilities was investigated. The oxygen content in Nb and Nb-X alloys was controlled by oxygen diffusion treatment at 1,100 °C using Nb/NbO mixture. Nb-aluminide, NbAl<sub>3</sub> and Nb<sub>2</sub>Al, layers were developed on the low-oxygen Nb substrate by an

aluminum diffusion treatment using Al/Al<sub>2</sub>O<sub>3</sub>/NH<sub>4</sub>Cl mixture at 1,100 °C; whereas an adhesive Al<sub>2</sub>O<sub>3</sub> scale developed on the Nb substrate with higher oxygen content. The alloy oxygen content decreased by an addition of Ta, Mo and Re, in this order, and the decrease in alloy oxygen content resulted in the transition of Al<sub>2</sub>O<sub>3</sub> formation from external scale to internal precipitates. This transition was not observed when low Al activity powder mixture, Ni<sub>50</sub>Al/Al<sub>2</sub>O<sub>3</sub>/NH<sub>4</sub>Cl, was used for Al diffusion process, and only external Al<sub>2</sub>O<sub>3</sub> scale was developed on all samples. In the present study, the effects of oxygen solubility limit, oxygen content, and the activity of Al in diffusion process on the formation of Al<sub>2</sub>O<sub>3</sub> scale will be discussed.

## **Effect of Water Vapor on the High-Temperature Oxidation of Pure Ni**

M. Auchi, S. Hayashi, K. Toyota, S. Ukai

Oxidation of Metals, 78, (2012) 51-61

The high-temperature oxidation behavior of pure Ni in air and Ar with and without 30 vol%H<sub>2</sub>O at 1,000 °C was investigated to understand the effects of water-vapor on the resulting oxidation kinetics and scale structures. It was found that water-vapor significantly affected the morphology and scale structure of NiO. A duplex NiO scale with a powder-like outer and dense inner NiO layer developed when the Ni was oxidized in atmospheres containing water-vapor. The grain size of the dense inner NiO layer was much smaller than that formed in dry atmospheres. The growth of the powder-like NiO required outward diffusion of Ni and its continued formation occurred at the interface between the powder and dense NiO layers. The dense inner NiO layer grew outward and incorporated the powder-like NiO particles and the resulting grain size of the inner layer was smaller in the presence of water-vapor. The water-vapor is speculated to have prevented sintering of NiO particles during growth of the NiO scale.

## **Effect of Fe and Partial Pressure of Oxygen on the Formation and Phase Transformation Behavior of Al<sub>2</sub>O<sub>3</sub> Scale**

S. Hayashi, Y. Takada, I. Saeki, A. Yamauchi, Y. Nishiyama, T. Doi, S. Kyo, and M. Sato

Materials and Corrosion, **63**, 862-868 (2012)

The effect of oxygen partial pressure on the phase transformation of  $\text{Al}_2\text{O}_3$  scale on various Fe–Al alloys with and without very thin ( $\sim 100$  nm) Fe coating was investigated. Fe-coating on Fe–Al alloys can effectively suppress metastable  $\text{Al}_2\text{O}_3$  formation, but little effect was observed when the samples were oxidized in a low partial pressure of oxygen. Under the low  $P_{\text{O}_2}$  atmosphere, metastable to stable  $\alpha\text{-Al}_2\text{O}_3$  scale phase transformation on both Fe-coated and non-coated Fe–Al alloys was significantly delayed. The lattice spacing of  $\alpha\text{-Al}_2\text{O}_3$  scale formed in air decreased with increasing alloy Al content. Further decrease in the lattice spacing of  $\alpha\text{-Al}_2\text{O}_3$  scale was observed when the alloy was oxidized in low  $P_{\text{O}_2}$ . The results obtained clearly indicated that the formation of  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}^{3+}$  in metastable  $\text{Al}_2\text{O}_3$  accelerated the metastable to stable  $\alpha\text{-Al}_2\text{O}_3$  scale transformation.

### **On the Early Stages of Scale Development on Ni-22Al-30Pt with and without Hf Additions at 1150 °C**

G. Smola, J. Jedlinski, B. Gleeson, S. Hayashi, J. Poussard, L. Grosseau, G. Bonnet, M. Nocun

Materials at high temperatures, **29**, 70-80 (2012)

Platinum modified Ni-Al-based alloys play an important role in the aeronautical industry as materials applied as Bond Coats (BCs) in thermal barrier coating systems (TBC), which provide protection against high temperature oxidation. Therefore, it is crucial for the assessment of the performance of the TBC to understand the oxidation behaviour of the Bond Coat material and the properties of the thermally grown oxide developing on it. This paper reports on the scale growth mechanism of Pt-modified  $\gamma'\text{-Ni}_3\text{Al}$ -based alloys with and without Hf additions at the early stages of oxidation. Samples were oxidized at 1150 C for up to 50 min. The consecutive stages of the scale evolution were followed by a systematic approach using a two-stage oxidation treatment in atmospheres containing different amounts of  $^{18}\text{O}_2$  oxygen isotope. The scale growth mechanism was followed with the aid of the in-depth analysis of elemental distribution, in

particular of the oxygen isotopes, across the scale using secondary ion mass spectrometry (SIMS). The surface morphology of the scales was observed using scanning electron microscopy, while its local phase composition was determined using photoluminescence spectroscopy. In addition, the imaging SIMS was used to generate distribution maps of the oxygen isotopes. Because of the limited lateral resolution of the SIMS technique (down to 0.5  $\mu\text{m}$ ) they were conclusive only for the most prolonged exposures (50 min). Typical stages of scale evolution were observed for the growing scales: initially flat layers were formed, followed by more or less developed blade-like surface grains, phase-transformation-related cracks and round patches and, finally, ridges. The latter were only found on the Hf-free material. The scale growth mechanism evolved from an initially predominant outward growth mechanism towards an increasing contribution of the inward mechanism. The relative extents of the outward and inward growth mechanisms depended strongly on the surface fraction of patches and through-scale cracks. The phase composition analyses showed that cracks and patches are regions where the transient aluminas were preferentially transformed into the  $\alpha\text{-Al}_2\text{O}_3$  phase, which is the required protective scale. The ridges formed in cracks essentially consisted of  $\alpha\text{-Al}_2\text{O}_3$ . For the most of studied exposure periods both types of phases: transient aluminas and  $\alpha\text{-Al}_2\text{O}_3$  co-existed in the scales. The results obtained indicate that: (i) phase transformations occur locally and not simultaneously in the entire scale; (ii) Hf additions retard the phase transformation; (iii) the phase transformation is completed only on Hf-free material and not after oxidation for 50 min; (iv) the two-stage oxidation approach should be carefully applied to study the growth mechanism of evolving scales in which regions of different phase compositions develop.





## 2013 Corrosion Research Seminar

March 8th, 2013 at Hokkaido University.

Professor Atsushi Nishikata, Tokyo Institute of Technology  
Electrochemical measurements under thin electrolyte solution and their application to the atmospheric corrosion

Dr. Hiroyuki Masuda, National Institute for Materials Science  
Importance of measurement technologies for elucidation of damage mechanism

Professor Fumio Watari, Hokkaido University  
Pilgrimage of materials --- from nuclear reactor to bio-system

Professor Toshiaki Ohtsuka, Hokkaido University  
Optical measurements in electrochemistry and corrosion science

