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Our research activities are concerned with corrosion and corrosion prevention of metals and molten salts electrolysis.

Research programs in progress are as follows:

Current topics on research are as following:

(1) New corrosion resistive films consisting of conductive polymers

A conductive polymer coating of polypyrrole (PPy) was applied to corrosion prevention of magnesium alloy, carbon steel and copper. The PPy layer was electrochemically prepared in aqueous electrolyte and the anions in the electrolyte was doped in conducting PPy.

The metals are passivated by the oxidative properties of PPy. If the anions in the electrolyte works as a stabilizer of the passive oxide, i.e., passivator, the passive oxide can stably exist and maintain the metals in the passive state for long time period. The selection of the doped anions is assumed to be most important.

The magnesium alloy was firstly covered by zinc electrodeposit and then by conducting polypyrrole (PPy) which was prepared in tartrate solution. The steel was coated by the PPy layer doped with various Mo and W poly-anions. The copper was covered the PPy layer including benzotriazole (BTA) inhibitor. The metals covered

with the PPy layer exhibited in NaCl aqueous solution a relative high potential corresponding to that in the passive state.

(2) 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.

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

Metallic Zr was electrodeposited on Cu substrate in LiCl-KCl-LiF molten salt containing ZrF_4 at 973 K. In voltammogram, cathodic current which corresponds to reduction reactions of Zr(IV) + 2e $\rightarrow$ Zr(II) and Zr(II) + 2e $\rightarrow$ Zr(0) were flowed at -1.4 and -1.6 V vs. Ag/Ag^+, respectively. The electrodeposition was performed by constant potential electrolysis from -1.4 to -1.6 V. The Zr was electrodeposited as $Cu_{10}Zr_7$ and CuZr on Cu substrate at -1.6V.

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

Glass plates were immersed in a molten salt of KNO_3-$AgNO_3$ 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.

(5) 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.

(6) Semiconducting properties of passive oxide on stainless steels (SS)

The semiconducting properties of passive oxides on Fe-Cr alloys was investigated by measurements of capacitance and Fe(IIII)/Fe(II) redox current. When the redox current was measured on the passivated alloys, tunneling of electrons occurs via the passive film from the alloy substrate to the electrolyte with Fe(III)/ Fe(II). The redox current decreased with higher content of Cr in the alloys. It may be connected with a homogeneous properties of the passive oxides which depends on the Cr enrichment in the oxide films.

(7) Oxidation of type 316L SS and nickel alloys under high temperature-high pressure water

Type 316L SS and nickel alloys of alloy 600 and alloy 690 were immersed in pure water under a circumstance of atomic power generators for a few months. The oxide films formed under the circumstance were studied by multiple-angle-of–incidence ellipsometry for the thickness, GD-OES for the depth profile, and Raman spectroscopy for the composition estimation.

For SS, the film consisted of two layers, the inner layer of which was composed of Cr-Fe spinel and the outer of α–Fe_2O_3.

For nickel alloys, Ni-Fe-Cr spinel oxides formed with thickness of several 10 nm. Initially Cr was enriched in the oxide and, however, the enrichment was gradually dissolved.

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

A fuel cell which consists of dissolution reaction of Al and reduction reaction of Cl_2 gas was arranged in 1-Ethyl-3-methylimidazolium chloride(EMIC) -$AlCl_3$ 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 at current density of 14 $mAcm^{-2}$. When the circuit was open, cell voltage quickly recovered to 2.3 V.

Other Activities:

Prof. Ohtsuka was invited from the 40th anniversary symposium of the Corrosion Science Society of Korea, Jeju, Korea April 28-29, 2011 and presented a paper entitled by "In-situ optical techniques for the corrosion study".

Assoc Prof. Ueda attended the 9th International Symposium on Molten Salt Chemistry and Technology, Trondheim, Norway, June 5-9 and 220th ECS meeting, Boston, USA, Oct.9-14, 2011, and presented a paper entitled by "Diffusion of Tl ion into the glass by ion exchange treatment" and "Evaluation of NaTFSI-TEATFSI ionic liquid as an electrolytic melt for Na electrorefining".

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

Presentations

Formation of Ag particles in the glass by molten salt ion exchange treatment, Y. Sakai, M. Ueda, T. Ohtsuka, T. Yamashita, Winter Meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 28, 2011

Al electroplating on Mg alloys in room temperature ionic liquid, S. Hariyama, M. Ueda, T. Ohtsuka, Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, February 1-2, 2011

Electrodeposition of Al-Sn alloys in $AlCl_3$-NaCl-KCl molten salt containing $SnCl_2$, R. Inaba, M. Ueda, T. Ohtsuka, Winter Joint Meeting of Hokkaido Branches of Chemistry-related Societies, Sapporo, February 1-2, 2011

Observation of thickness change of passive film by polarized reflection microscope, K. Yamanaka, M. Ueda, T.Ohtsuka, Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, February 1-2, 2011

Electroplating of Al on AZ121 Mg alloy in ionic liquid of room temperature, S. Hariyama, M. Ueda, T. Ohtsuka, The 123st Meeting of The Surface Finishing Society of Japan, Kantougakuin University, Yokohama, March 17-18, 2011

Electrodeposition of Al-Sn alloys in low temperature chloride molten salt, R. Inaba, M. Ueda, T. Ohtsuka, Spring Meeting of ECSJ 2011, Yokohama National University, Yokohama, March 29-31, 2011

Electrochemical property of NaTFSI-TEATFSI mixture ionic liquid, K. Honda, M.

Ueda, T. Ohtsuka, 2011 Spring Meeting of Jpn. Inst. Metals, Tokyo Urban University, Tokyo, March 25-27, 2011

Diffusion of Tl ion into the glass in ion exchange treatment, M. Ueda, H. Matsunaga, T. Ohtsuka, 9th International symposium on molten salts, Trondheim, Norway, June 5-9, 2011

Electrodeposition of Al-Sn alloys from low temperature molten salt, R. Inaba, M. Ueda, T. Ohtsuka, Summer Session of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 23, 2011

Output characteristic of Al-Cl_2 cell in room temperature ionic liquid, H. Matsunaga, M. Ueda,T. Ohtsuka, Summer meeting 2011 of Hokkaido branch of The Chemical Society of Japan, Muroran Institute of Technology, Muroran, July 24, 2011

Development of Al-Cl_2 battery in EMIC-$AlCl_3$ ionic liquid, H. Matsunaga, M. Ueda, T. Ohtsuka, 62nd Annual meeting of ISE, Toki messe, Niigata, September 16, 2011

Electroplating temperature for Al plating on Mg alloy in $AlCl_3$-EMIC ionic liquid, S. Hariyama, M. Ueda, T. Ohtsuka, 62nd Annual meeting of ISE, Toki messe, Niigata, September 16, 2011

Development of Zn-Mg coating by PVD, W. Murakami, M. Ueda, T. Ohtsuka, 62nd Annual meeting of ISE, Toki messe, Niigata, September 16, 2011

Formation process of polypyrrole film on zinc covering AZ91D alloy, N. Sheng, T. Ohtsuka, 62nd Annual meeting of ISE, Toki messe, Niigata, September 16, 2011

Potential modulation reflectance of passivated type 303 stainless steel, 62nd Annual meeting of ISE, T. Ohtsuka, Y. Sasaki, A. Hyono, Toki messe, Niigata, September 16, 2011

Oxygen reduction of Pd electrodes covered by platimum monolayers, T. Ohtsuka, Y. Sugawara, M. Ueda, 62nd Annual meeting of ISE, Toki messe, Niigata, September 16, 2011

In situ observation of heterogeneity on thin titanium passive oxide film by micro-ellipsometry, A. Hyono, K. Yamanaka, M. Ueda, T. Ohtsuka, 62nd Annual meeting of ISE, Toki messe, Niigata, September 16, 2011

Electrorefining reaction of Na in TEATFSA-NaTFSA ionic liquid, M. Ueda, K.

Honda, T. Ohtsuka, EPTM 2011, Kyoto University, Kyoto, September 18, 2011

Electrodeposition of Al-Sn alloys in $AlCl_3$-NaCl- KCl molten salt containing $SnCl_2$, M. Ueda, R. Inaba, T. Ohtsuka, EPTM 2011, Kyoto University, Kyoto, September 18, 2011

Potential dependence of Al-Sn alloys in $AlCl_3$-NaCl- KCl molten salt containing $SnCl_2$, R. Inaba, M. Ueda, T. Ohtsuka, The 124th meeting of The Surface Finishing Society of Japan, Nagoya University, Nagoya, September 21, 2011

Corrosion prevention of 55%Al-Zn coated steel by bi-layer polypyrrole film, N. Sheng, H. Ryu, M. Ueda, and T. Ohtsuka, The 55th Japan Conference on materials and Environments, Nagoya, Japan, September 28-30,2011

Corrosion protection of copper by polypyrrole film including BTA, Y. Lei, A. Hyono, M. Ueda, T. Ohtsuka, The 55th Japan Conference on materials and Environments, Nagoya, Japan, September 28-30,2011

Evaluation of NaTFSI-TEATFSI ionic liquid as an electrolytic melt for Na electrorefining, M. Ueda, K. Honda, T. Ohtsuka, 220th ECS meeting, Westin hotel, Boston, USA, October 9-14, 2011

Electrodeposition characteristic of Na in NaTFSI-TEATFSI ionic liquid, K. Honda, M. Ueda, T. Ohtsuka, The 149th Fall meeting of the Japan institute of metals, Okinawa convention center, Ginowan, November 7, 2011

Development of Mg alloy coating by PVD and improvement of corrosion resistance of steel, W. Murakami, M. Ueda, T. Ohtsuka, The 149th Fall meeting of the Japan institute of metals, Okinawa convention center, Ginowan, November 7, 2011

Corrosion of SUS 316L loaded by stress under high-pressure and high-temperature water, Y. Hamaguchi and T. Ohtsuka, The 149th Fall meeting of the Japan institute of metals, Okinawa convention center, Ginowan, November 7, 2011

In situ observation of heterogeneous growth of thin titanium oxide film by a micro-ellipsometer, A. Hyono, K. Yamanaka, M. Ueda, T. Ohtsuka, The 149th Fall meeting of the Japan institute of metals, Okinawa convention center, Ginowan, November 7, 2011

Purity of refined Na by electrorefining in NaTFSI-TEATFSI ionic liquid, K. Honda, M. Ueda, T. Ohtsuka, The 43rd Symposium on Molten Salt Chemistry, Osaka

University, Osaka, November 22, 2011

Corrosion protection of metals by conducting polypyrrole film, T. Ohtsuka, 2011 International Joint Symposium between CNU & Hokkaido Univ. on Advanced Material Science & Technology, Cungnam National University, Daejeon, Korea, November 1-4, 2011

Corrosion protection of steels by conducting polypyrrole layer, T. Ohtsuka, Memorial Symposium for Olin Padadium Award of Prof. Koji Hashimoto “Materials Science for the Sustainable World”, Tohoku University, Sendai, Japan, November 12-13, 2011

Semiconductor property of passive film on Fe-Cr alloys, M. Abe, A. Hyono, M. Ueda, T. Ohtsuka, Corrosion Dream 2011, Osaka University, Osaka, December 2, 2011

Role of Co in enhanced activity of synthesized electrocatalysis for oxygen reduction reaction by electrochemical deposition, M. Li, A. Hyono, M. Ueda, T. Ohtsuka, Corrosion Dream 2011, Osaka University, Osaka, December 2, 2011

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Dr Alexander Mozalev, stayed from October 2010 as a JSPS fellow, left on March after conducting interesting research on anodizing of bilayer valve metal films for fabrication of unique nanostructured oxide films.

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, corrosion, passivation and surface finishing.

Current topics on research are as following:

(1) Proton-conducting oxide nanofilms

Gas-tight silicate and phosphate nanofilms have been prepared by spin coating and proton conductivity in the nanofilms have been examined after depositing gold or platinum button electrode. The nanofilms showed efficient proton conductivity, and interestingly, the conductivity was enhanced markedly by reducing the film thickness to less than ~100 nm. Such scaling behavior has been analyzed in terms of a percolation model. We also found efficient proton-conducting anodic ZrO_2-WO_3 and ZrO_2-WO_3-SiO_2 films even below 200ºC. Using these proton-conducting nanofilms, we are trying to fabricate an intermediate temperature fuel cell.

(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, Ti-Si alloys, 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. 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 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. Advanced process using physical vapor deposition has now been investigated to develop a porous electrode for electrolytic capacitor application. Utilization of substrate with cellular structure is effective to tailor alloy nano-columns with controlled gaps between columns. Our findings revealed high potential of porous non-equilibrium Ti-Si alloys prepared by PVD technique for capacitor application. Further, Marked enhancement of capacitance of the anodic zirconia by incorporation of silicon and aluminum species was achieved and novel design for capacitor materials was proposed.

(4) 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.

(5) 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:

In September, Prof. H. Habazaki worked as a coordinator of the Symposium "Corrosion and Surface Treatments", which was held as one of the Symposia of 62nd Annual ISE Meeting (Niigata, Japan). He also organized the Symposium "Materials Science for the Sustainable World" in Commemoration of Professor Koji Hashimoto, a Recipient of 2011 ECS Olin Palladium Award at Sendai in November. Prof. H. Habazaki attended IUMRS-ICA2011, held in Taipei in September and presented an invited lecture entitled "Capacitance Enhancement by Formation of Nanocomposite Anodic Oxides for Electrolytic Capacitors". He also presented an invited lecture "Proton-conducting nanofilms for intermediate temperature fuel cells" at the 3rd Symposium of FoE-HU & MRC-ETHZ at Zurich in October.

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, 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 μHz to 32 MHz.
Contact angle meters: Kyowa Interface Science, Dropmaster system, to evaluate superhydrophobicity of solid surface.
Q-mass: Balzers Quadstar421 system for mass analysis of gases with mass number of less than 200.

Presentations

Hiroki Habazaki, Shu Yang, Yoshiaki Taguchi, Yoshitaka Aoki, Masanobu Teraoka, Tsuji Etsushi, “Formation of Porous Anodic Oxide Films on Valve Metals in Hot Phosphate-glycerol Electrolyte”, 62nd ISE Annual Meeting, 11-16 September, Toki Messe, Niigata (2011)

Alexander Mozalev, Hiroki Habazaki, Jaromir Hubalek,“The superhydrophobic properties of self-organized nanostructured surfaces derived from anodically oxidized Al/Nb and Al/Ta metal layers”, 62nd ISE Annual Meeting, 11-16 September, Toki Messe, Niigata (2011)

Masahiro Seo, Yoshitaka Aoki, Hiroki Habazaki, Masayuki Inaba, Mitsutoshi Yokomizo, Takazumi Hayakawa, Takenori Nakayama, “In-situ X-ray Absorption Spectroscopy of Pb Species Adsorbed on Ni in Acidic Perchlorate Solution”, 62nd ISE Annual Meeting, 11-16 September, Toki Messe, Niigata (2011)

E. Tsuji, K. Fukui, A Imanishi, "Influence of Surface Roughening of Rutile TiO_2 Single Crystal on Photocatalytic Activity for oxygen Evolution in Acidic and Alkaline Solutions", 62nd ISE Annual Meeting, 11-16 September, Toki Messe, Niigata (2011)

Shu Yang, Etsushi Tsuji, Yoshitaka Aoki, Hiroki Habazaki, Anodizing of Magnesium in Hot Phosphate-glycerol Electrolyte, 62nd ISE Annual Meeting, 11-16 September, Toki Messe, Niigata (2011)

Ke Ye, Yoshitaka Aoki, Shinji Nagata, Hiroki Habazaki, “Enhanced Thermal Stability and Proton Conductivity of Anodic ZrO_2-WO_3 Nanofilms by Incorporation of Silicon Species”, 62nd ISE Annual Meeting, 11-16 September, Toki Messe, Niigata (2011)

H. Habazaki, S. Koyama, Y. Aoki, “Capacitance Enhancement by Formation of Nanocomposite Anodic Oxides for Electrolytic Capacitors”, IUMRS-ICA2011: 12th International Conference in Asia, 19-23 September, Taipei World Trade Center Nangang Exhibition Hall, Taipei (2011)

H. Habazaki, K. Ye, D. Kowalski, Y. Aoki, E. Tsuji, “Proton-conducting nanofilms for intermediate temperature fuel cells”, The Third Symposium on Academic Exchange and Collaborative Research between the Faculty of Engineering, Hokkaido University (FoE-HU) & the Materials Research Center, ETH Zurich (MRC-ETHZ), 13 October, ETHZ, Zurich (2011)

T. Fujii, E. Tsuji, Y. Aoki and H. Habazaki, "Fabrication of superoleophobic surfaces with dual-scale roughness, The Third Symposium on Academic Exchange and Collaborative Research between the Faculty of Engineering, Hokkaido University (FoE-HU) & the Materials Research Center, ETH Zurich (MRC-ETHZ), 13 October, ETHZ, Zurich (2011)

H. Habazaki, "Proton-conducting amorphous nanofilms at intermediate temperatures", Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ.-Univ. Electron. Sci. Tech. China Joint Symposium Materials Science and Nanotechnology for the 21st Century, 21-23 December, Univ. Electron. Sci. Tech. China, Chengdu, China (2011)

K. Ye, Y. Aoki, E. Tsuji, S. Nagata, H. Habazaki, "Thickness dependence of proton conductivity of anodic ZrO_2-WO_3-SiO_2 nanofilms", Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ.-Univ. Electron. Sci. Tech. China Joint Symposium Materials Science and Nanotechnology for the 21st Century, 21-23 December, Univ. Electron. Sci. Tech. China, Chengdu, China (2011)

LABORATORY OF HIGH TEMPERATURE MATERIALS

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Research work at “Laboratory of high temperature materials” directs toward 1) high-temperature corrosion of Cr-Si-Ni and CoNiCrAlY alloys, 2) high-temperature corrosion of stainless steels in simulated coal-firing environments, 3) oxidation of Fe-Si steels in N_2-H_2 atmosphere, 4) high temperature oxidation of various metal disilicides, 5) sintering of nano WC-X, 6) hydrogen production using H_2O-NaOH-stailess steel system, and 7) development of Pb-free solders,.

Current topics on research are as following:

(1) High-temperature corrosion of SiO_2-foming alloys

High-temperature corrosion tests of Cr-Si-Ni and CoNiCrAlY-Si alloys in molten Na_2SO_4 and NaCl salts and gaseous O_2-Na_2SO_4-NaCl atmospheres are being carried out. Especially, the SiO_2 formers showed excellent corrosion resistance. The result demonstrates that the SiO_2 scale is very effective for preventing internal sulfidation and chlorination of alloys.

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

environments

In order to clarify the effects of Cr content, temperature, and CO_2 on local attack (internal sulfidation and carburization), high temperature corrosion tests of some stainless steels were carried out in simulated coal-firing environments. The results are as follows; (1)local-internal attack in substrate occurs in both of low and high CO_2 atmospheres, (2)the local attack in somewhat severe in the low CO_2 atmosphere and in lower temperature corrosion, (3)the structure of the locally-attacked area is outer scale(Fe oxide)/(Cr, Fe) oxide/(Cr oxide+Cr sulfide+Si oxide)/substrate, (4)the local attack is probably caused by generation of defect (cracking) in a Cr_2O_3 scale, (5) increase of Cr content in steel leads to suppression of local attack, and (6) carburization does not probably occur even in the high CO_2 atmosphere.

(3) Oxidation of High Si steels in N_2-O_2-H_2O and N_2-H_2 atmospheres

High Si steels (base steel and steels with 0.1, 0.3 or 0.5mass% Mo) were oxidized in a N_2-3%O_2-20%H_2O atmosphere at 1150ºC. The oxidation kinetics showed that base steel has the highest weight gain. In contrast, 0.5Mo has the lowest weight gain. The scale thickness decreased as Mo content increased. Distribution of alloying elements showed that Mo 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. In addition, annealing of Fe-Si steels in N_2-H_2 (dew point: -65 C) at 900 C is being carried out and relationship between change of surface morphology of the steels and Si content is being investigated.

(4) High temperature oxidation of Nb-Si-Ge intermetallics

To improve oxidation resistance of Nb-Si intermetallics, Ge was added into Nb-Si intermetallics and the influence of Ge addition on the oxidation resistance was investigated. Ge addition didn't lead to the formation of additional phases in substrate. Ge addition into Nb_5Si_3 did not result in the improvement of oxidation resistance. On the other hand, oxidation resistance of $NbSi_2$ was remarkably improved by Ge addition more than 3mass% due to the formation of a low viscosity silica layer.

(5) Sintering of nano WC powders

The sintering kinetics of nano grained tungsten carbide (*n*-WC) powders has been analyzed by non-isothermal and isothermal sintering. Non isothermal sintering experiments revealed a multi staged sintering process in which at least three major sub-stages can be distinguished. The isothermal shrinkage strain also exhibited an asymptotic behavior with time indicating an end point density phenomenon in most of the temperature ranges. Although grain growth and densification in conventional WC powders generally obey an inverse relation to each other, in *n*-WC powders both can act synergistically to increase the net densification rate.

(6) Development of new hydrogen production method

As a new method for the production of hydrogen, the $NaOH/H_2O$/metal 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.

(7) Development of new Pb-free solders

The influences of composition and cooling rates on the microstructures of Sn-Ag-Cu solders solidified at different cooling rates were clarified. An increase in Ag content causes coarsening of Sn-Ag_3Sn eutectic phase. On the other hand, increasing cooling rate led to grain refinement. Moreover, the addition of Bi resulted in further refinement of primary and Sn-Ag_3Sn eutectic phases. The interfacial reactions between Cu substrate and molten lead-free solders were also clarified.

Other Activities:

In March, Prof. Kurokawa and Dr. A. K. Nanda Kumar attended The 4th International Workshop on Plasma Application and Hybrid Functionally Materials in Melbourne, Australia, and presented papers entitled “The Development of High Functional-Heat Resistant Materials Using Gas Tunnel Type Plasma Spraying” and “Microstructural Evolution of Sintered Nano WC-Si Compacts”. In July, Prof. Kurokawa attended The 2nd JCOAL-NETL Oxyfuel Workshop in Albany, OR, U.S.A., and presented a paper entitled “High Temperature Corrosion Behavior of Boiler Tube Materials -Structure and Analysis of Scale-”. In September, Prof. Kurokawa and Dr. A. K. Nanda Kumar attended The Inter’l Symposium on Applied Plasma Science ’11 in Hakone, Japan, and presented a paper entitled “Effect of Boron on the Microstructure of Spark Plasma Sintered Ultrafine WC”.

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

Structure of oxide scales formed on Al-Mg alloys in H_2O-containing atmospheres; K. Kurokawa: 2nd NIMS-Hokkaido Univ. Joint Symp. on Corrosion, Sapporo, Jan. 2011.

Influence of primary nucleation frequency on Ag_3Sn in solidification of Sn-Ag-Cu-X alloys; S. Kirai, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa, and J. Tanaka: Mate 2011, Yokohama, Feb. 2011.

Relationship between growth rate of interfacial reaction layer and carbon content in solder /carbon steel system; T. Kawamoto, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa, and J. Tanaka: Annual JIEP Meeting, Tokyo, March 2011.

Microstructural evolution of sintered nano WC-Si compacts; A. K. Nanda Kumar, M. Watabe, and K. Kurokawa: The 4th International Workshop on Plasma Application and Hybrid Functionally Materials, Melbourne (Australia), March 2011.

Fundamentals of high-temperature corrosion -high-temperature corrosion of metals and alloys-; K. Kurokawa: The 54th JSCE Seminar, Tokyo, April 2011.

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: DIMAT, France, July 3-8, 2011.

High temperature corrosion of Cr-Si-Ni alloys in gaseous O_2- Na_2SO_4-NaCl; T. Sano, T. Sudiro, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: Annual Meeting of 123 Committee of Jpn. Promotion of Sci., Tokyo, July 2011.

High Temperature Corrosion Behavior of Boiler Tube Materials- Structure and Analysis of Scale -, The 2nd JCOAL-NETL Oxyfuel Workshop, Albany(OR), USA, July 14, 2011

Effect of MoO_3 addition on mechanical properties of Cr_2O_3 scale; K. Ohtani and K. Kurokawa: The Summer Joint Meeting of The Hokkaido Secs. Of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July 2011.

Hydrogen production in H_2O-NaOH-stainless steel reaction system; S. Yoshida, T. Mizuno, and K. Kurokawa: ibid.

Effect of Ge addition on oxidation resistance of $NbSi_2$; K. Kimura and K. Kurokawa:

ibid.

Effect of Boron on the Microstructure of Spark Plasma Sintered Ultrafine WC; A. K. Nanda Kumar, M. Watabe, and K. Kurokawa: Inter'l Symp. on Applied Plasma Science '11, Hakone, Sept. 2011.

High Temperature Corrosion Behavior of STBA21 Alloy in Na_2SO_4+25.7mass%NaCl Atmosphere; T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: The 58th Symposium on Materials and Environments, Nagoya, Sept. 2011.

Improvement of oxidation resistance of $NbSi_2$ by Ge addition; K. Kimura and K. Kurokawa, The 148th Annual Meeting of Jpn. Inst. Metals, Naha, Nov. 2011.

Hydrogen production in the H_2O-NaOH-stainless steel system using metal particle; S. Yoshida, T. Mizuno, and K. Kurokawa: ibid.

High-temperature Corrosion of CoNiCrAlY-Si Alloys in the Liquid Phase of Na_2SO_4-NaCl; T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: ibid.

High temperature corrosion of metals and alloys in atmospheres containing mixed oxidants: K. Kurokawa : Invited lecture in Tohoku Sec. of ISIJ, Akita, Dec. 2011.

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. Junnichiro 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 following:

(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-1β, IL-8, TNF-α, 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 10μm. 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 psuedopodium 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 0.5 mm with the multiple fiber structure has been fabricated by either drawing of fiber-polymer complex at 250C or photopolymerization method. Biocompatible CaO-P_2O_5-SiO_2-Al_2O_3 (CPSA) glass fibers of 8-20μm 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 1-100μm and macroscopic cylindrical Ti implant in μm 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 1-3μm 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 superoxided anion(O^{2-}) sing human neutrophils showed that Ni solution has he 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-α, was not detected in any solution of Ni, V, Ti, the simulated body fluid(Hank's solution) mixed with 10mm particles of Ti and with submicron size Ni particles. TNF-α was found only in the 1-3μm 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 1-3μm and 10μm Ti particles suggests that the particles(1-3mm) smaller than cell size(about 5mm in neutrophils) induces cytotoxicity as a result of phagocytosis, while for particles larger than cell size(10mm) 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 prosthoses 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 polymmerization 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, γ-ray from Co60 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 polymmerization 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)

Yttria partially stabilized zirconia (YPSZ) ceramic is suitable for dental and medical use because of it's 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 2μm 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 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 sesitization 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 TiO_2 in contrast to very little effect in an untreated 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 form 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 expulsed. 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.Lu Xiong of Southwest Jiaotong University, China joined to our laboratory on

October 2009 as the postdoctoral researcher of the Japan Society for Promotion of Science (JSPS) for the development of nano-structured scaffold for medical and biochemical applications.
The international collaborations are continued with Institute of Dental Materials Science, Umea University, SWEDEN (Emerita Prof. Maud BERGMAN) on application of Ti, ZrO_2, 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 Gravitometry and Differential Thermal Analysis(TG/DTA) : Rigaku Denki
Diamond Cutter : Buehler and Struers diamond cutter

Presentations

Cell Proliferation on Carbon Nanotubes Coated Dishes in Different Cell Lines, Tsukasa AKASAKA, Makoto MATSUOKA, Atsuro YOKOYAMA, Takeshi HASHIMOTO, Fumio WATARI, the 40th the Fullerenes and Nanotubes General Symposium, Nagoya, Mar.8-10, 2011

Cell Proliferation on Carbon Nanotubes Coated Dishes in Different Cell Lines, Tsukasa AKASAKA, Shigeaki ABE, Motohiro UO, Fumio WATARI, International Dental Materials Congress 2011, Soul, May.27-29, 2011

Cell Culture on Thin Films of Carbon Nanotubes, Tsukasa AKASAKA, Makoto MATSUOKA, Atsuro YOKOYAMA, Takeshi HASHIMOTO, Fumio WATARI, the 9th Annual Meeting of Society of Nano Science and Technology, Sapporo, Jun.2-4, 2011

Cell Proliferation on Carbon Nanotubes Coated Dishes in Different Cell Lines, Tsukasa AKASAKA, Shigeaki ABE, Motohiro UO, Fumio WATARI, the 3rd International Symposium on Surface and Interface of Biomaterials, Sapporo, Jul.12-15, 2011

A DFT and MD study on interaction of water molecules with graphene, S. Abe, Y. Nagoya, F. Watari, H. Tachikawa; ISPlasma2011, Nagoya, Mar. 2011

SEM observation of carbon nanotubes scaffold using ionic liquids; S. Abe, A. Hyono, F.Watari, T. Yonezawa; The Japanese Society of Microscopy, Fukuoka, May 2011

Biodistribution of micro-/nano-sized particles and their cytocoxisity, S. Abe, N. Iwadera, K. Ishikawa, S. Itoh, T. Akasaka, M. Uo, Y. Yawaka, Y. Kuboki, T. Yonezawa, F. Watari; International Dental Materials Congress 2011, Seoul, May 2011

Morphology, size distribution and elemental analysis of several dental working debris, S. Abe, N. Iwadera, M. Esaki, K. Aoyama, T. Akasaka, M. Uo, M. Morita, Y. Yawaka, F. Watari; 3rd International Conference on Surface and Interface of Biomaterials, Sapporo, Jul. 2011

Morphlogy and photophysical properties of one-dimensional arrayed porphyrin

aggregates assisted by cyclodextrin inclusion complexation, S. Abe, H. Kobayashi, T. Kiba, F. Watari, S. Sato; KJF2011,
Gyeongiu, Sep. 2011

Biocompatibility and biodistribution of poly (lactic acid)-coated micro/nano particles, S. Abe, A. Sasaki, N. Iwadera, T. Akasaka, M. Uo, F. Watari; International Union of Materials Research Society-Internatonal Conference in Asia 2011, Taipei, Sep. 2011

Development of a novel SEM observation method using an ionic liquid; S. Abe, A. Hyono, T. Akasaka, F.Watari, T. Yonezawa; The Japanese Society of Dental Materials and Devices, Kouriyama, Oct. 2011

A DFT and MD Study on Interaction of Water Clusters with Nano Carbon Materials, S. Abe, Y. Nagoya, F.Watari, H. Tachikawa; PVSEC21, Fukuoka, Oct. 2011

Internal diffusion of biocompatible polymer-coated inorganic nanoparticles in mice, S. Abe, A. Sasaki, T. Narushima, Y. Uchida, T. Akasaka, M. Uo, T. Yonezawa, F. Watari; 23rd International Symposium on Ceramics in Medicine, Istanbul, Nov. 2011

Biodistribution and cytocompatibility of micro/nano-sized ceramics particles: an in vivo and in vitro
investigation, S. Abe, N. Iwadera, T. Akasaka, M. Uo, Y. Yawaka, Y. Kuboki, T. Yonezawa, F. Watari; 11th Asian BioCeramics Symposium, Tsukuba, Dec. 2011

Rapid and non-destructive analysis of metallic dental restorations using X-ray fluorescence spectra and light-element sampling tools; K. Furuhasi, M. Uo, Y. Kitagawa, F. Watari, The 3rd International Symposium on Surface and Interface of Biomaterials, Sapporo, July 12 (Tuesday)-15 (Friday), 2011

Application of Carbon Nanotube Coated 3D Scaffold for Bone Tissue Engineering.; E. HIRATA, M. UO, F. WATARI, A. YOKOYAMA, International Dental Materials Congress 2011, Seoul, Korea May 28, 2011

Bone formation in carbon nanotube-coated collagen sponge with cultured osteoblasts; E. HIRATA, M. UO, F. WATARI, A. YOKOYAMA, The 3rd International Symposium Surface and Interface of Biomaterials 2011, Sapporo, Japan, July 13-15, 2011

Development of the Carbon nanotube-coated anodized titanium; S. INOUE, M. UO, E. HIRATA, M. HO LEE, T. SUNG BAE, F. WATARI, A. YOKOYAMA, International Dental Materials Congress 2011, Seoul, Korea May 28, 2011

Surface modification of anodized titanium with Carbon Nanotubes and its in vitro compatibility ; S. INOUE, M. UO, E. HIRATA, M. HO LEE, T. SUNG BAE, F. WATARI, A. YOKOYAMA, The 3rd International Symposium Surface and Interface of Biomaterials 2011, Sapporo, Japan, July 13-15, 2011

LABORATORY OF ADVANCED HIGH-TEMPERATUER MATERIALS

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The research activities of the laboratory are directed to the development of the advanced high strengthened ODS alloys, and 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) Nano-meso structure control of 9Cr-ODS ferritic steels

Nano-meso structure of the 9Cr-ODS ferritic steels can be successfully controlled by the α–γ phase transformation, and their high-temperature creep strength is the most superior worldwide in the class of ferritic tubes. This is owing to existence of the residual ferrite phase within the tempered martensite phase. In our group, the formation mechanism of the residual ferrite and the origins of its superior strength are intensively investigated through synthesizing ODS alloys by ball-milling and their analyses by means of nano-indentation measurement, differential thermal analysis, high-temperature X-ray diffraction, SEM and TEM observation. Moreover, extremely high strength keeping ductility has been recently attained by means of hot-rolling.

(2) Texture control of 12Cr-ODS ferritic steels

The appropriate cold-rolling and heat-treatment processes are being investigated for the manufacture of 12Cr-ODS ferritic steels, focusing on the texture revolution. A measurement technique by FE-SEM/EBSP (Electron Back Scattering Pattern) is mainly applied in this study. Cold-rolling of the sheet induces strong α-fiber texturing

composed of {111}～{001}<110> parallel to the rolling direction and rolling plane. Recrystallization of the cold-rolled sheet takes place at elevated temperatures beyond 1100°C. The formation mechanism of the recrystallized texture, typically {011}<001>, was investigated; this unique texture was revealed to exist within shear bands of the cold-rolled structure. This finding suggests that the recrystallized grains are nucleated during the stage of cold-rolling, and are selectively grown at temperatures beyond 1100°C.

(3) Development of Ni-based, Co-based ODS superalloys and bubble dispersion strengthened alloys

Basic study for development of the Ni based ODS superalloys is being conducted. It was found that mechanical alloying (MA) induces nano-crystal formation of in 50nm size in the Ni-Y_2O_3 system, and the nano-size grains are maintained up to 1300℃. Beyond this temperature, recrystallization and grain-growth takes place due to coarsening of Y_2O_3 oxide particles. A study for making extremely fine distributions of oxide particles is being also conducted for Al-added Ni-based ODS superalloys; the effective elements for fine oxide particle distribution were discovered and a patent application was conducted. Co-Al based ODS alloys are being investigated from a viewpoint of making composite-like materials by means of spinodal decomposition of Al. Nano-bubble dispersion strengthened alloy is also synthesized by using thermally decomposed gases from PMMA.

(4) Effects of water vapor on internal oxidation of Ni-low Al alloys

The effects of water vapor on internal oxidation of Ni-low Al alloys are being investigated. Water vapor apparently increased the initial growth rate of internal oxidation zone, when the outer NiO was formed. However, little effect on the growth of internal oxidation zone was found without the external NiO formation.

(5) Effect of Fe coating on the phase transformation of Al_2O_3 scale during high temperature oxidation

The effect of very thin (~50nm) Fe coating on FeAl alloys is still being investigated. In-situ X-ray diffraction measurements of oxide scale formation and growth by means of synchrotron radiation confirmed that the α-Al_2O_3 scale precipitated from Al saturated Fe_2O_3. Very clear double peaks from α-Al_2O_3 indicated that Fe saturated α-Al_2O_3 was initially formed and subsequent formation of relatively pure-α-Al_2O_3 occurred. This in-situ measurement confirmed the “sympathetic nucleation” of α-Al_2O_3 scale from the corundum crystal of Fe_2O_3.

(6) Effect of Mn on the phase transformation of FeO formed on Fe-Mn alloys

Effect of isothermal Phase transformation of FeO was investigated. Formation of magnetite seam at the scale/alloy interface was found to delay with Mn. The time for

complete transformation was also delayed significantly with Mn. The lamellar spacing of Fe/Fe_3O_4 eutectoid structure also increased with increasing Mn content in FeO. Apparently Mn addition slows down the isothermal transformation of FeO. Due to larger lamellar spacing, Mn was considered to decrease the decomposition temperature of FeO.

(7) Effect of phosphors on the internal oxidation of Si in Fe-Si-P ternary alloys

Effect of phosphors on the internal oxidation of Si in Fe-low Si-P alloys were investigated at the temperatures from 800 to 1300°C. Internal Fe_2SiO_4 and SiO_2 layers were formed in this order from the surface. At higher temperatures more than 1200°C, liquid phase formation was confirmed in the outer Fe_2SiO_4 layer. P-Si-Fe oxide precipitates were found to form at the outer part of internal oxidation zone and the formation of Film-like internal SiO_2 precipitates were confirmed in ternary alloys. Growth rate of internal oxidation zone were tended to decrease with increasing P content. Significant P-depletion was observed in the internal oxidation zone, and the concentration gradient of P and Si was found to cross over in the internal oxidation zone. Based on the result, P addition was considered to increase the outward Si diffusion flux, resulting in growth rate of internal oxidation zone slower.

Presentations

Effects of Two-Step Cold Rolling on Recrystallization Texture in Cold Rolled ODS Ferritic Steels: B. Leng, T. Narita, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2011

Creep Deformation Behavior of ODS Ferritic Steel: Y. Sugino, S. Hayashi, S. Ukai, T. Kaito and S. Ohtsuka: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2011

Synthesize of Fe-basis BDS Alloy by means of Thermally Decomposed Gases: R. Kohno, Y. Sugino, S. Hayashi and S. Ukai: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2011

Grain Boundary Deformation in ODS Ferritic Steel: Y. Sugino, N. Oono, S. Hayashi, S. Ukai, T. Kaito and S. Ohtsuka: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Effect of Hot-Rolling on the Mechanical Properties in 9CrODS Steels: Y. Kudo, S. Ukai, S. Hayashi, T. Kaito and S. Ohtsuka: The Summer Joint Meeting of Hokkaido

Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Charpy Impact Properties of 9CrODS Ferritic Steels: W. Izawa, S. Ukai, S. Hayashi, N. Oono, T. Sakamura and Y. Kohno: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Effect of Oxide Particle Distribution on Recrystallization in Cold Rolled ODS Ferritic Steels: B. Leng, S. Ukai, N. Oono, S. Hayashi, S. Ohtsuka and T. Kaito: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Hardness and Micro-Texture in Friction Stir Welds of a Nanostructured ODS Ferritic Steels: W. Han, S. Ukai, F. R. Wan, H. Numata, N. Oono, S. Hayashi and Y. Sato: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Structure Control and High Temperature Strength Improvement by Hot-Rolling in 9CrODS Ferritic Steels: R. Miyata, S. Ukai, N. Oono, S. Hayashi, S. Ohtsuka, T. Kaito, T. Azuma and S. Ohsaki: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Microstructure Control of Co-Basis ODS Alloys: K. Takezawa, S. Ukai, N. Oono, S. Hayashi: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2011.

Corrosion Behavior of 9CrODS Steels by Simulated Fission Products (Cs, Te): Y. Yamazaki, S. Ukai, N. Oono and S. Hayashi: The Autumn Meeting of Atomic Energy Society of Japan, Jpn. Kita-Kyusyu, Japan, Sep., 2011.

Charpy Impact Properties of 9CrODS Ferritic Steels: W. Izawa, S. Ukai N. Oono and S. Hayashi: International Conference on fusion Reactor Materials, Charleston, South Carolina, Oct., 2011.

Effect of Cooling Rate from Hot-Rolled Condition on Tensile Properties in 9CrODS Ferritic Steels: T. Kudo, S. Ukai, R. Miyata, N. Oono, S. Hayashi, T.Kaito and S.Otsuka: International Conference on fusion Reactor Materials, Charleston, South Carolina, Oct., 2011.

Strength Correlation with a Residual Ferrite Fraction in 9CrODS Ferric Steels: R. Miyata, S. Ukai, N. Oono, S. Hayashi, T. Kaito and S. Otsuka: International Conference on fusion Reactor Materials, Charleston, South Carolina, Oct., 2011.

Development of 15CrODS ferritic Steels over 1,000 ºC Operation: Y. Sawazaki, S. Ukai, N. Oono, S. Hayashi, K. Hamajima and A. Niwa, International Conference on fusion Reactor Materials, Charleston, South Carolina, Oct., 2011.

High Temperature Deformation Mechanism of Recrystallized ODS Ferritic Steels: Y. Sugino, S. Ukai, N. Oono, S. Hayashi, Q. Tang, B. Leng, T.Kaito and S.Otsuka: International Conference on fusion Reactor Materials, Charleston, South Carolina, Oct., 2011.

Creep and Tensile Properties of Hot-Rolled 9CrODS Ferritic Steels: S. Ukai, R. Miyata, Y. Sugino, N. Oono, S. Hayashi, T. Azuma, T. Kaito and S. Otsuka: International Conference on fusion Reactor Materials, Charleston, South Carolina, Oct., 2011.

Effect of Oxide Particle Distribution on Recrystallization in Cold Rolled ODS Ferritic Steels: B. Leng, S. Ukai, N. Oono, S. Hayashi, S. Ohtsuka and T. Kaito: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Corrosion Behavior of Fe-base Model Alloys by Simulated Fission Products (Cs, Te): Y. Yamazaki, S. Ukai, N. Oono and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Oxide Particle Refinement in 4.5 % Al Ni-based ODS Superalloys: Q. Tang, N. Oono, S. Ukai and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Microstructure Control of Co-base ODS Alloys: K. Takezawa, N. Oono, S. Ukai and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Improved High-Temperature Strength by Hot-Rolling in 9CrODS Ferritic Steels: R. Miyata, N. Oono, S. Ukai, S. Hayashi, S. Ohtsuka and T. Kaito: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Synthesis of Fe-Base Nano Bubble Distribution Strengthened (BDS) Alloys by Means of PMMA Decomposed Gases: R. Kawano, N. Oono, S. Ukai, S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Cold-Rolling and Recrystallization Mechanism of ODS ferritic steels: B. Leng, S. Ukai, N. Oono, S. Hayashi, S. Ohtsuka and T. Kaito: 123 Committee Meeting for Heat Resistant Alloys, Tokyo, Japan, Nov. 2011.

Oxide Particle Refinement in Al Added Ni-base ODS Superalloys: Q. Tang, N. Oono, S. Ukai and S. Hayashi: 123 Committee Meeting for Heat Resistant Alloys, Tokyo, Japan, Nov. 2011.

Effect of Oxygen in the Alloy on the Formation of External Protective Oxide Scale: S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Formation of Al_2O_3 Scale on Nb-O Alloys by Al Diffusion Process: R. Yamagata, S. hayashi, S. Ukai, and T. Narita: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

High-Temperature Oxidation of Ni in Water Vapor: K Toyota, S. Hayashi, S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Effect of Alloy Al Content on The Phase Transformation Behavior of Al2O3 Scale Formed on Fe-Al Alloys: Y. Takada, S. Hayashi, and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Okinawa, Japan, Nov., 2011.

Formation of Protective Al_2O_3 Scale on Low-Al Niobium Alloys by a Two-Step Oxygen-Aluminum Diffusion Treatment: S. Hayashi, S. Takagi, R. Yamagata, T. Narita, and S. Ukai: 8th International Conference on Diffusion in Materials, Dijon, France, July, 2011.

Isothermal Transformation Behavior of FeO Scale: S. Hayashi, K. Mizumoto, S. Ukai, Y. Kondo, H. Tanei: The Autumn Meeting of Iron and Steel Inst. Jpn, Osaka, Japan, Sep., 2011.

In-situ Measurement of Phase Transformation Behavior of Al_2O_3 Scale: S. Hayashi. Y. Takada, et al.,: The Annual Meeting of Corrosion Engineering, Nagoya, Japan, Sep., 2011.

Compositional and Environmental Factors Affecting Al_2O_3 Scale Transformation: S. Hayashi: Gordon Research Conference, High-Temperature Corrosion, New London, NH, USA, July, 2011.

LABORATORY OF ECO-PROCESSING

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Prof. Ryosuke O. Suzuki merged as the professor of the laboratory of Eco-processing from Kyoto University on March 2006. He 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 interesting topics when the electrolysis of CaO in the molten $CaCl_2$ is applied. The electrolysis of CO_2 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 our member as an associate professor from laboratory of interface microstructure 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 $CaCl_2$

Reduction of the oxides of titanium, vanadium, niobium and tantalum are studied when the CaO dissolved in the molten $CaCl_2$ 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 using the evolved gas analysis. CO_2 gas reduction gets the current interest in the morphology of precipitated carbon particles.

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

Micro- and Nano-lens array made of anodic alumina were fabricated by laser irradiation, imprint, and electrochemical techniques such as anodizing and electrochemical dissolution. Fabrication of lens-like micro- and nano-structures on aluminum surface was realized by laser irradiation, imprint, and anodizing in acidic solutions such as oxalic, sulfuric, and phosphoric acids. The specimens were anodized again to form the oxide film on the structures, and then aluminum substrate was dissolved in $SnCl_4$ solution. Many micro- and nano-meter sized lenses can be successfully fabricated, and further investigation of the optical characteristics should be done in order to apply these lens array in the micro- and nano-optical devices.

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 elecrtrolysis.

(2) Hot thermocouple method for oxide solidification

Hot thermocouple supports the melt as well as temperature monitoring. The solidification was directly observed at 900-1200C through the optical microscope, and the effect of purged gas was studied when considering the recycling of the oxide slag for desulfization.

Prof. R.O. Suzuki was invited at 9^{th} International Symposium on Molten Salt Chemistry and Technology, and presented the keynote lecture on"Ionic Conduction of Oxygen and Calciothermic Reduction in Molten CaO-$CaCl_2$". Prof. R.O. Suzuki was invited at the International Symposium on Materials Science for Sustainable Society – Eco-materials and Eco-innovation for Global Sustainability (ECOMATES 2011). He talked on the molten salt electrolysis supported by thermoelectric generation using solar light.

The following foreign scientist visited this laboratory : Prof. Dr. Geir Martin Haarberg and Dr. Morten A. Onsrud, Norwegian University of Science and Technology, Trondheim, Norway. Ms. Li Ronghua, University of Science and Technology Beijing (USTB), China, as a special research student.

Facilities and Capabilities

X-ray diffractmeter: Philips X'Pert Pro. A set for thin film XRD and powder XRD, and another set for high temperature XRD using Pt heating planer stage or Al_2O_3 crucible with RF heating.
Oxygen and Nitrogen Analyzer: LECO TC-600. Inert gas extraction with carbon crucible and infrared absorption method. 5mass%-0.05 mass ppm. The previous set was replaced to the most modern.
Sulfur and Carbon Analyzer: LECO CS-600. Carbon and nitrogen are converted to CO and NO gas by burning in O_2 gas with RF heating and they are detected by the infrared absorption method. 6mass%-0.6 mass ppm. The previous set was replaced to the most modern.
CO/CO_2 Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 10 vol%.
NO/SO_2 Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 2 vol%.
Constant voltage generators: Takasago Electrics. 4 sets. Max.50V and 20 A.
High voltage amplifier: Takasago Electrics. 100V-8000V.
Ozone gas generators: 2 sets. max 8 vol%O_3 gas using O_2 gas.
Thermal Analyzers: SII EXSTAR-6000 TG/DTA. With Pt heater up to 1500C.
Thermal Conductivity Measuring Unit: Kyoto Electrics. Hot disk method at room temperature.

Presentations

Preparation of Nb-Ti-Ni alloy powder using the molten $CaCl_2$ and its deoxidation; R. Enmei, T. Kikuchi and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan. 2011.

Powder formation of niobium by the molten salt electrolysis and reduction in $CaCl_2$ melt; I. Ueda, R.O. Suzuki, and T. Kikuchi : ibid.

Carbon formation from CO_2 gas using molten salt electrolysis; K. Otake, H. Kinoshita, T. Kikuchi and R.O. Suzuki : ibid.

Reduction of SO_2 gas using molten salt electrolysis in $CaCl_2$; H. Nishiyama, H. Kinoshita, T. Kikuchi and R.O. Suzuki : ibid.

Fabrication of micro-circuit board with aluminum and its oxide; S. Fujita, T. Kikuchi, and M. Sakairi : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Chem. Soc., Sapporo, Feb. 2010.

Reduction of titanium oxides using electrolysis in molten CaO-$CaCl_2$, N. Kobayashi, K. Kobayashi, T. Kikuchi and R.O.Suzuki, Annual Meeting of Iron and Steel Inst. Jpn, Tokyo, March, 2011.

Development of micro-circuit fabrication process with aluminum and its oxide; T. Kikuchi, S. Fujita, and M. Sakairi : The 123th Annual Meeting of Surf. Finsh. Soc. Jpn., Tokyo, March 2010.

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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:

Current topics on research are as following:

(1) Development of new surface coating methods for Mg alloy.

Mg alloys are attractive material because of their light weight, high strength and rich resource in nature. However, their weak corrosion resistivity limits the 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 metal plating with optimized zincate pretreatment. Electroplating of Al on AZ91D from ionic liquid bath of EMIC has been also established because a coating of corrosion resistive less-noble Al on Mg alloy can prevent the strong galvanic coupling of plating layer with the substrate and thus can suppress selective corrosion of substrate. Many previous reports on this subject have revealed the difficulty in formation of a highly adhesive Al coating on Mg alloys. We therefore applied zincate pretreatment combined with Cu pre-deposition technique to AZ91D alloy o obtain an uniform Al plating layer with strong adhesivity.

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

Copper is one of candidates for metal container used for depository of radioactive nuclear wastes produced in atomic power plants to be stored deep-underground to separate them from civilian areas. Corrosion rate of Cu foil immersed in the solution simulating underground water at high temperature was monitored by using a temperature-compensated resistometry developed in this laboratory. Corrosion rate of Cu depended strongly on ionic species contained in the electrolytes with 0.001 M level, temperature and dissolved oxygen concentration. Suppression of corrosion rate was also found in the solution containing small amount

of dissolved silica. Morphology of corrosion products were strongly affected by the kind of species in the solutions. Elemental analysis of corrosion products was also conducted by using FT-IR and XPS.

(3) Development of pH sensors durable for high temperature measurement.

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, durability or operation temperature. pH sensitive Ir oxide electrode with 0.2 mm in diameter was therefore prepared by anodic oxidation. pH sensitivity and durability of the fabricated electrodes were evaluated as a function of immersion time in a hot water up to 80 °C. Ir oxide electrodes showed good pH sensitivity and durability after long term immersion up to 1 month. Even if the electrode was degraded, re-anodization of the electrode could recover the pH sensitivity. Another pH sensitive sensor composed of Ir oxide powder, PTFE powder and carbon powder was also evaluated.

(4) Analysis of micro-plasma formed in aqueous electrolyte solution

High voltage in an order of kV was applied to two electrodes immersed in electrolyte solutions to form a micro-plasma in a narrow gap placed between two electrodes in the solution. The gap was a small hole of 0.2 to 1.0 mm in diameter made in a glass plate or a fused quartz plate. Temperature elevation of local solution forms a small vapor bubble in the gap due to focusing the heat generation of the Ohmic loss in the solution. Applying high voltage to the vapor phase ignited micro-plasma formation. Not only direct applying a high voltage to the electrodes immersed in the solution, but also applying a high ac voltage (30 kHz, ca. 9 kV) to dielectric electrodes which were not directly contacted to the solution can form a micro-plasma. The later system has an advantage to eliminate the detrition of the electrodes and the contamination of the solution due to plasma sputtering. Spectroscopic analysis of the light emitted from a micro-plasma reveals that the plasma was non-equilibrium state of electron at a temperature in the order of 10^4 K and OH^- ions at a temperature of several thousand K.

(5) Application of multichannel electrode system to the atmospheric corrosion of steel

Many corrosion phenomena proceed in a non-uniform manner and the galvanic coupling of different areas in the corroding system sometimes determines the actual corrosion feature. In order to measure directly the coupling current in the actually corroding system the multichannel electrode system has been developed and applied to many corrosion system. For analysis of atmospheric corrosion of steel we developed a 100 channel electrode system and applied it to an array electrode in an

arrangement of 10 x 10 matrix composed of 100 piece of iron rod of 0.5 mm in diameter embedded in resin. The array electrode was exposed to wet and dry cycling test with dropping a droplet containing NaCl on the surface to initiate corrosion. Galvanic couple was clearly observed between the corroding electrodes and the other electrodes. To investigate the function of Zn coating in the corrosion protection, Zn was electroplated on four electrodes at the center of the array electrode. Sacrificial anodic current on Zn-plated electrode and successive suppression of coupling current on the electrodes covered with Zn corrosion products were clearly observed.

(6) Optimization of discharging condition of Al-air battery

Combination of anodic dissolution of less-noble metals and cathodic reaction of oxygen reduction in air have been considered as a electric source named metal-air battery. Al is a candidate for anodic material due to its high energetic density provided by light weight and tri-valency of ions. Efficient dissolution reaction of Al in the alkaline solution should be proceeded for low internal resistance at large current supply during the operation period. On the other hand, dissolution reaction should be suppressed during the idle period. Self-discharging, i.e., self dissolution reaction of Al electrode coupled with hydrogen evolution reaction should be also suppressed in the both periods. To control the dissolution reaction rate of Al in these conditions small amount of Zn^{2+} ions were added to alkaline solution. Substitution reaction of Al dissolution and Zn deposition formed a thin Zn layer on Al surface and suppressed the undesired Al dissolution. Suitable concentration of Zn^{2+} concentration, bath temperature and discharging modes were examined as a function of energetic efficiency of Al as an active material in the operation / idle cycling test.

Presentations

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J. Yajima, K. Azumi: In-situ measurement of corrosion behavior of Cu in the underground depository environment, *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 following:

(1) Flowing-type Micro-droplet-cell for Micro-fabrication of Titanium Surface

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.

(2) Microfabrication of Multichannel Microelectrode-array with Microscratching and Electroless Plating

Scanning probe technique such as an SECM enables to visualize the electrochemical activity on a specimen electrode. However it is not suitable to pursuit the relatively rapid reaction of the electrode such as an initiation of pitting corrosion. In order to overcome this problem, a microelectrode-array has been fabricated tentatively by using microscratching method and electroless nickel plating. A micropattern of nickel is selectively plated on a scratched part of an insulating coating covered with a glass substrate plate. The suitable conditions for pretreatment of the plating as well as the scratching are discussed to obtain a well-ordered pattern.

(3) Grain-dependent Passive State of Iron Single Grains in Sulphuric Acid

Single grains of pure iron were dynamically polarised in 0.05 mol dm^{-3} sulphuric acid using a micro-capillary cell. Polarisation curves for single grains revealed that the passivity-maintaining current strongly depended on crystallography of the surface.

No fluctuation in the current was observed on 0 0 1 grain, but small and large fluctuations corresponding to the surface depassivation-repassivation were observed on 1 0 1 and 1 1 1 grains, respectively. The depassivation seems to be due to breakdown of the passive film induced by compressive stress in the film and slip of the surface microstructure formed during the active dissolution prior to the passivation.

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

In order to investigate the mechanism and kinetics of growth or degradation of anodic oxide film on pure titanium surface, a set of macro lens and CCD camera was combined on an ellipsometer. Under a null ellipsometric condition, potentiodynamic polarization of the specimen in sulfuric acid resulted in the deviation from the initial condition and enabled to observe the specimen surface depending on a surfacial crystallography, indicating that the grain-dependent growth of an anodic oxide film on the polycrystalline specimen. In bromide-concentrated solution, a series of film breakdown and pitting propagation was observed by using the ellipsometric microimaging.

Other Activities:

In September, Dr. Koji Fushimi attended to Eurocorr 2011 held in Stockholm, Sweden, and presented the paper entitled “Heterogeneous dissolution of polycrystalline pure iron in sulphuric acid solution”. Dr. K. Fushimi also attended to the 62nd Annual Meeting of the International Society of Electrochemistry held in Niigata, Japan, and presented the paper entitled “Anisotropic corrosion of polycrystalline pure iron in H_2SO_4”. In November, Dr. K. Fushimi attended to the 18th International Corrosion Congress held in Perth, Australia, and presented the paper entitled “SECM observation of polycrystalline iron corroding in sulphuric acid solution”.

Presentations at International Symposia

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K. Fushimi, K. Matsushita, K. Miyamoto, Y. Hasegawa, Anisotropic corrosion of polycrystalline pure iron in H_2SO_4, 62nd Annual Meeting of the International Society of Electrochemistry, Niigata, Sep. 11–16 (2011).

M. Seo, K. Fushimi, Y. Aoki, H. Habazaki, M. Inaba, M. Yokomizo, T. Hayakawa, T. Nakayama, In-situ X-ray Absorption Spectroscopy of Pb Species Adsorbed on Ni in Acidic Perchlorate Solution, 62nd Annual Meeting of the International Society of Electrochemistry, Niigata, Sep. 11–16 (2011).

K Fushimi, K Matsushita, H Tachikawa & Y Hasegawa, SECM observation of polycrystalline iron corroding in sulphuric acid solution, 18th ICC, Perth, Nov. 20-24 (2011).

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Dr. S. Ningshen (Indira Gandhi Centre for Atomic Research, Kalpakkam India) joined our grope as a JSPS postdoctoral research fellow from July 2011. Research work of our group directs toward 1) formation of novel of oxide film for dielectric materials and anticorrosion films by anodizing and LPD, 2) development of new solution flow type micro-droplet cell and its application, and 3) establishment of localized corrosion mechanism of aluminum alloys and stainless steels, 4) Development of micro electrochemical technique for detection of permeated hydrogen formed during corrosion, and 5) corrosion behavior of 11 mass% Cr F/M steel, ODS steel and titanium alloys in corrosive solutions

Current topics on research are as following:

(1) Hydrophobic porous alumina films and its corrosion resistance

A low wettability surface can be formed on aluminum by anodizing and desiccation treatment. Samples subjected to gradual heating and cooling desiccation exhibit a larger contact angle (CA) than samples subjected to fast heating and cooling desiccation in an oven at the same temperature. From the SEM and AES observations, the low CA surface shows a regular porous morphology, and there is little change in the surface chemical composition before and after the desiccation treatment. According to electrochemical corrosion tests, samples with higher CA show a better corrosion resistance than either the anodized sample or the low CA samples in NaCl solution. According to the interface model, the regular porous structure in the anodic oxide films would play the main role to increase CA and inhibit corrosion reactions. It is also shown that anodizing time can also influence surface wettability of desiccated porous type anodic oxide film formed on aluminum.

(2) High capacitance composite oxide film formed on aluminum by liquid phase

deposition treatment and anodizing

Liquid Phase Deposition treatment (LPD) was also applied to form a high capacitance titanium dioxide film on aluminum. Addition of sucrose to LPD solution changes capacitance of formed TiO_2/Al_2O_3 composite layer. The maximum capacitance was observed at 0.4 kmol m^{-3} sucrose addition.

(4) Anodic oxide film formed locally by Sf-MDC

A solution resistance reduced solution flow type micro-droplet cell with co-axial dual capillary tubes, Sf-MDC, was applied to form porous type anodic oxide film at selected area on aluminum without masking. This technique makes it possible to form anodic oxide film locally, and the thickness increases with increasing substrate temperature without any local film break down. The film thickness rate at 323 K is about ten times faster than that of at 283 K and the current during oxide film formation is also increased with increasing substrate temperature. This result suggests that oxide film dissolution at the bottom of the pore is accelerated by substrate temperature.

(5) Effect of CH_3COONa on corrosion and surface film of 13Cr stainless steel in simulated oilfield environments

The effects of concentration of CH_3COONa on electrochemical behavior and surface film structure of low C - 13%Cr stainless steel were examined. The passive current region (steady value of polarization curves) became wider by addition of CH_3COONa. Addition of CH_3COONa also changed immersion corrosion behavior. From XPS surface analysis, addition of CH_3COONa may change oxide film structure and thickness, and this lead to widen the passive current region.

(6) Corrosion of aluminum allay in model tap water -focused on metal cations-

The hardness of metal cation based on HSAB theory was applied to explain an influence of metal cations in model tap water on corrosion behavior of A3003 and highly pure aluminium. Both immersion and galvanic corrosion rate can be explained by hardness of metal cations. From XPS and AES analysis, hard metal cations are incorporated in surface oxide film to increase corrosion resistance of substrate.

(7) Development of μ-electrochemical technique for simultaneous measurement of rest potential and permeated hydrogen generated by wet-dry cycle corrosion tests.

Permeated hydrogen shows very important role in hydrogen embrittlement, however, traditional electrochemical cell technique is not suitable for detection of hydrogen generated at damaged area of coated layer on steel. Simultaneous measurement of permeated hydrogen volume and rest potential technique was developed. The developed small cell makes it possible to measure rest potential and hydrogen permeation current during wet/dry corrosion test, and the accuracy is about

several nA. The hydrogen permeation current detected only scratched specimen, and the estimated detection efficiency is about 10 %. The hydrogen permeation current of scratched specimen increases with increasing scratched area, and its increases with decreasing rest potential.

(8) Corrosion Resistance and Passive Film Characterization of Oxide Dispersion Strengthened ferritic Steels in Acidic and Chloride Environments

Oxide Dispersion Strengthened (ODS) ferritic steels are high performance structural material being developed for future high temperature energy production technologies. However, the most important issue for the application of ODS steel is to understand their corrosion resistance behavior in different environments. Corrosion resistance and passive film characteristic of ODS ferritic steel in different acidic and chloride media were evaluated. 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 borate, H_2SO_4 and HNO_3 media but shift in corrosion potential was observed with increase in concentration. However, in acidic-chloride and chloride media low pitting potential and high anodic dissolution was observed. XPS analyses of the pre-passivated and after polarization surface indicated that the oxides are mostly composed of Fe_2O_3, Cr_2O_3 along with Y_2O_3 and very little of Ti, W and Ni elements.

Other Activities:

In September, Assoc. Prof. Sakairi attended EUROCORR2011 at Stockholm Sweden presented a paper entitled "Effect of magnesium ions on corrosion behaviour of A3003 in simulated tap water" Assoc. Prof. Sakairi, Mr. K Otani and S. Takagi attended the 62nd ISE Annual Meeting at Nigata. Mr. Otani presented a paper entitled "Effect to Kind of Cations to Corrosion Behavior of A3003-H24 in Model Tap Water" and Mr. Takagi presented a paper entitled "Development of μ-electrochemical technique for detection of permeated corrosion generated hydrogen".

In November, Assoc. Prof. Sakairi attended 2011 International Joint Symposium between CNU& HU Advanced Material Science & Technology at Daejeon, Korea and presented a paper entitled "Atmospheric corrosion behavior of model cut-edge formed pre-painted zinc alloy coated steels". Assoc. Prof. Sakairi attended 18th ICC at Parth, Australia and presented a paper entitled "Influence of Cations on Corrosion Behavior of Aluminum Alloys in Drinkable Water and Model Tap Water".

Facilities and Capabilities

AFM: SII SMP AFM with solution cell.

Confocal scanning laser microscope Laser Tech. Co. 1SA-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

Presentations

Effect of temperature and dissolved oxygen on corrosion of 13Cr stainless steel in high concentration NaCl, J. Tatehara, M. Sakairi and S. Hasizume, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, Jan., 2011.

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Effect of cations on corrosion behavior of A3003 in model tap water, K. Otani, M. Sakairi and A. Kaneko, ibid.

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Effect of magnesium ions on corrosion behaviour of A3003 in simulated tap water, M. Sakairi], K. Otani, A. Kaneko, Y. Seki and D. Nagasawa, EURROCORR2011, Stkholm, September, 2011.

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Area selective anodizing by Sf-MDC and its application, M. Sakairi, T. Murata, K. Fushimi and T. Kikuchi, The 149 Autumn meeting of Japan Inst. Metal, Okinawa, November, 2011.

Surface analysis of A3003 after immersed in different cation containing solutions, M. Sakairi and K. Otani, The autumn meeting of Light Metal Soc., Tokyo, November, 2011.

Influence of Cations on Corrosion Behavior of Aluminum Alloys in Drinkable Water and Model Tap Water, M.Sakairi, A. Kaneko, K. Otani, Y. Seki and D. Nagasawa, 18th ICC, Parth, November, 2011.

Composition Change in Al3Ni2 Microchannel Lining Layers by Alkali Leaching, Y. Saito, T. Ohmi, M. Sakairi and M. Iguchi, 6th International Symposium on Advanced Science and Technology in Experimental Mechanics, Osaka, November, 2011.

Anodic Oxidation of Al-Zn Alloy Lining Layer Produced by a Sacrificial-Core Method, M. Ishida, T. Ohmi, M. Sakairi and M. Iguchi, ibid.

Structure Control of Cu-Zn Microchannel Lining Layers with Potentiostatic Dissolution, K. Kobayashi, T. Ohmi, M. Sakairi and M. Iguchi, ibid.

ABSTRACT of PUBLICATIONS

Corrosion Protection of Steel Materials by Conducting Polymer

T. Ohtsuka

Electrochemistry, **79**, 959-963 (2011)

The corrosion protection of steels by conducting polymer coating was reviewed. The conducting polymers such polypyrrole, polyaniline and polythiophen play a role of oxidant, and coating of the conducting polymer induces passivation of substrate steels. When the conducting polymer remains enough oxidation capability, the substrate steels exhibits passivation and is protected by the passive oxide underneath the conducting polymers. When one designs the doping anions in the conducting polymer, the conducting polymer reveals a self-healing properties, in which the passive state was spontaneously repaired, if the film was damaged. (Japanese)

Electrodeposition of Al-Pt alloys using constant potential electrolysis in $AlCl_3$-NaCl-KCl molten salt containing $PtCl_2$

M. Ueda*, H. Hayashi and T. Ohtsuka

Surface and Coatings Technology, **205**, 4401-4403, (2011)

To form Al-Pt alloys for high temperature coatings, molten salt electrolysis was attempted with a $AlCl_3$-NaCl-KCl molten salt containing $PtCl_2$ at 448 K. The voltammogram showed cathodic reduction of Pt ions to start at a potential of 1.4 vs. Al/Al(III) in the molten salt. Deposition of pure Pt was possible at 1.2 V and there was co-deposition of Al and Pt at potentials more negative than 1.0 V. The co-deposit was a mixture of intermetallic compounds of $AlPt_2$ or $AlPt_3$. The ratio of the Pt in the electrodeposits decreased with increasingly negative potentials from 100 at% at 1.2 V to 25 at% at 0.0 V.

Diffusion of Tl ion into the glass by ion exchange treatment

M. Ueda, H. Matsunaga, T. Ohtsuka and T. Yamashita

Proceedings of 9th International Symposium on Molten salt, 101-106 (2011)

To make functional glasses, glass immersed in $TlNO_3$-KNO_3 molten salt at 753 K for various time periods, where the ion exchange is done between Na ions in the glass and Tl ions in the molten salts. The Tl ions embedded in the glass were then reduced to metallic Tl nano-particles by hydrogen gas at 803K for 1h. The depth of the ion exchange layer to 150 μm in the glass was found to be proportional to a square root of the immersion time period. It was suggested that the ion exchange process is controlled by a diffusion of Tl ions from the surface to the inner. Reduction of Tl ions to metallic Tl in hydrogen gas occurred only the surface region thinner than 4 μm. The concentration profile of metallic Tl is discussed from the nucleation-nucleus growth and the diffusion of Tl ions from the deeper area

Thin film fuel cell based on nanometer-thick membrane of amorphous zirconium phosphate electrolyte

Y. Aoki, Y. Fukunaga, H. Habazaki and T. Kunitake

Journal of the Electrochemical Society, **158**, B866-B870 (2011)

Novel thin film fuel cell based on the 100 nm-thick electrolyte of amorphous $ZrP_{2.6}O_x$, working at 400°C, was demonstrated. The hydrogen permeable membrane fuel cell (HMFC) using a Pd foil as a nonporous solid anode was fabricated. Ni interlayer of several hundreds nm thickness was introduced between the Pd anode and the $ZrP_{2.6}O_x$ electrolyte in order to suppress the deterioration of the electrolyte nanofilm by the deformation of the Pd anode during hydrogen absorption. In the $ZrP_{2.6}O_x$ electrolyte the transport no. of proton was unity at 400°C as detd. by an EMF measurement. The modification of the Ni anode surface by an ultrathin Pt or Pd layer effectively decreased the anode/electrolyte interfacial polarization. Consequently, the HMFC revealed the OCV of 1.0 V and the max. power d. of 1.8 mW cm^{-2} at 400°C.

Power-law scaling of proton conductivity in amorphous silicate thin films

Y. Aoki, H. Habazaki and T. Kunitake

Solid State Ionics, **192**, 93-96 (2011)

Amorphous hafnium silicate, a-$Hf_{0.1}Si_{0.9}O_x$, thin film with thickness of 32, 41, 55, 80, 110, 120, 180 and 320 nm was prepared by multiple spin-cast process and the proton conductivity across the films was measured at intermediate temperatures

(100-400 °C) in dry atmosphere. The morphologically- and compositionally-uniform films were prepared on a substrate as confirmed by SEM, RBS and XPS measurements. a-$Hf_{0.1}Si_{0.9}O_x$ thin film clearly revealed the H/D isotope effect on ionic conductivity, indicating that protonic conduction is dominant in the measured temperature range. The films did not reveal thickness-dependent proton conductivity in dry air and the [sigma] at given temperatures is almost constant at any thickness. No increment of [sigma] in a-$Hf_{0.1}Si_{0.9}O_x$ thin films by reduction of thickness might be related to the absence of the highly-conductive acid network with mesoscopically-sized length because of the relatively low concentration of Brønsted acid sites inside films.

Finite size effect of proton-conductivity of amorphous silicate thin films based on mesoscopic fluctuation of glass network

Y. Aoki, H. Habazaki, S. Nagata, A. Nakao, T. Kunitake and S. Yamaguchi

Journal of the American Chemical Society, **133**, 3471-3479 (2011)

The finite size effect of proton cond. of amorphous silicate thin films, a-$M_{0.1}Si_{0.9}O_x$ (M = Al, Ga, Hf, Ti, Ta, and La), was studied. The proton cond. across films, σ, was measured in dry air by changing the thickness at 10-1000 nm σ of the films with M = Al, Ga, and Ta was elevated in a power law by decreasing thickness into less than a few hundred nanometers, and the increment was satd. at a thickness of several 10's of nanometers. However, σ of the films with M = Hf, Ti, and La was not related to the decrease of the thickness in the range of >10 nm. Thickness-dependent cond. of the former could be numerically simulated by a percolative resistor network model that involves the randomly distributed array of two kinds of resistors R1 and R2 (R1 > R2) as a simple cubic-type lattice. High-resoln. TEM clarified that a-$M_{0.1}Si_{0.9}O_x$ films involved heterogeneous microstructures made of the condensed domain and the surrounding uncondensed matrix due to the fluctuation of glass networks on the nanometer scale. The condensed domain had a wormlike shape with an av. length of several 10's of nanometers and performed the role of the proton conduction pathway penetrating through the poorly conducting matrix. The thickness-dependent cond. could be identical to finite-size scaling of the percolative network of the interconnected domains in the nanometer range.

Proton-conductivity of amorphous aluminum phosphate thin films under anhydrous conditions

Y. Aoki, S. Hirata and H. Habazaki

Journal of the Electrochemical Society, **158**, P41-P44 (2011)

The proton conductivity sigma across 100 nm thick, amorphous aluminum phosphate thin films under anhydrous conditions was investigated. The densely packed glass films were uniformly formed without formation of pinholes and clacks over the electrode substrate by multiple spin-coating with a mixed precursor sol, as checked by transmission electron microscopy. X-ray absorption spectroscopy, and Fourier transform infrared indicated that the Al-rich films were mainly composed of alumina and phosphate mixed glass phase, but the P-rich films involved a large amount of the aluminum metaphosphate glass moiety. sigma abruptly changed with Al/P ratio owing to this variation of glass network structure. The Al-rich films revealed the large activation energy Ea of about 1.0 eV, but the P-rich films revealed the small Ea of about 0.2 eV above 200 ℃ and they kept the value on the order of 10^{-5} S cm^{-1} at the temperatures. Consequently, the sigma of P-rich films were one order of magnitude higher than that of the others at around 300 ℃.

Fabrication of Super-Oil-Repellent Dual Pillar Surfaces with Optimized Pillar Intervals

T. Fujii, Y. Aoki and H. Habazaki

Langmuir, **27**, 11752-11756 (2011)

Hierarchical dual pillar surfaces with optimized pillar intervals are fabricated by a novel combined process of the c oblique angle magnetron sputtering deposition of Al-Nb alloys and their anodizing. The pillar intervals are controlled by the deposition angle and cell size of a scalloped substrate for oblique angle deposition. Anodizing of the deposited pillar surfaces develops a nanopillar oxide layer, producing the hierarchical dual pillar surfaces. After being coated with a fluoroalkyl phosphate layer to reduce the surface free energy, hierarchical surfaces with submicrometer pillar intervals greater than 400 nm show super liquid repellency even for hexadecane with a low surface tension of 27.5 mN m^{-1}, although the submicrometer pillar surfaces with smaller submicrometer pillar intervals and without nanopillars were not super-oil-repellent. In contrast, the dual pillar surfaces show superhydrophobicity regardless of the submicrometer pillar intervals. Thus, the present study demonstrates

the importance of the pillar intervals (gap size between pillars) to realize the superoleophobicity.

Superhydrophobic hierarchical surfaces fabricated by anodizing of oblique angle deposited Al-Nb alloy columnar films

T. Fujii, Y. Aoki and H. Habazaki

Applied Surface Science, **257**, 8282-8288 (2011)

A combined process of oblique angle magnetron sputtering and anodizing has been developed to tailor superhydrophobic surfaces with hierarchical morphology. Isolated submicron columns of single-phase Al-Nb alloys are deposited by magnetron sputtering at several oblique deposition angles on a scalloped substrate surface, with the gaps between columns increasing with an increase in the deposition angle from 70° to 110°. Then, the columnar films have been anodized in hot phosphate-glycerol electrolyte to form a nanoporous anodic oxide layer on each column. Such surfaces with submicron-/nano-porous structure have been coated with a fluoroalkyl phosphate layer to reduce the surface energy. The porous surface before coating is superhydrophilic with a contact angle for water is less than 10°, while after coating the contact angles are larger than 150°, being superhydrophobic. The beneficial effect of dual-scale porosity to enhance the water repellency is found from the comparison of the contact angles of the submicron columnar films with and without nanoporous oxide layers. The larger submicron gaps between columns are also preferable to increase the water repellency.

Mechano-electrochemistry of a passive surface using an in situ micro-indentation test

K. Fushimi, T. Shimada, H. Habazaki, H. Konno and M. Seo

Electrochimica Acta, **56**, 1773-1780 (2011)

Depassivation-repassivation of iron surfaces in boric-borate solutions were investigated by using the micro-indentation test. A pair of current peaks due to repair of the passive film following rupture of the film were observed during a series of indenter drives, i.e., loading and unloading of the indenter. The shape of the current peak depended on environmental conditions (conductivity and pH of the solution) and

substrate conditions (mechanical processing history, alloyed element) as well as indentation conditions (repetition, maximum depth, and maximum load). Plastic deformation of the surface was accompanied by surface depassivation, while no depassivation occurred during the elastic deformation, indicating that the passive film on iron has a ductile property. The solution conditions did not affect the scale of depassivation but affected the rate of repassivation. Dislocations in the substrate made surface depassivation difficult but enhanced reactivity during the repassivation. The test also revealed that type-312L stainless steel has high corrosion resistance in a concentrated NaCl solution.

Incorporation and migration of phosphorus species within anodic films on an Al-W alloy

S.J. Garcia-Vergar, I.S. Molchan, F. Zhou, H. Habazaki, D. Kowalski, P. Skeldon and G.E. Thompson

Surface and Interface Analysis, **43**, 893-902 (2011)

The effect of tungsten species on the incorporation and migration of phosphorus species within anodic alumina is investigated. The study employs barrier anodic films, formed on a sputtering-deposited Al-15at.% W alloy in phosphate electrolytes. The films consist of either an outer tungsten-containing region and an inner tungsten-free region, or a tungsten-containing region only. Phosphorus species are shown to migrate inward in the tungsten-containing alumina more slowly than in the tungsten-free alumina. In contrast, the outward migration of tungsten species is relatively unaffected by the presence of phosphorus species. The relevance of the results to the use of tungsten tracers for the study of porous film growth is discussed.

Enhanced capacitance of composite anodic ZrO_2 films comprising high permittivity oxide nanocrystals and highly resistive amorphous oxide matrix

H. Habazaki, S. Koyama, Y. Aoki, N. Sakaguchi and S. Nagata

ACS Applied Materials & Interfaces, **3**, 2665-2670 (2011)

Anodic oxide films with nanocrystalline tetragonal ZrO_2 precipitated in an amorphous oxide matrix were formed on Zr-Si and Zr-Al alloys and had significantly enhanced capacitance in comparison with those formed on zirconium metal. The capacitance

enhancement was associated with the formation of a high-temperature stable tetragonal ZrO_2 phase with high relative permittivity as well as increased ionic resistivity, which reduces the thickness of anodic oxide films at a certain formation voltage. However, there is a general empirical trend that single-phase materials with higher permittivity have lower ionic resistivity. This study presents a novel material design based on a nanocrystalline-amorphous composite anodic oxide film for capacitor applications.

Formation and dielectric properties of anodic oxide films on Zr-Al alloys

S. Koyama, Y.Aoki, S. Nagata and H. Habazaki

J. Solid State Electrochemistry, **15**, 2221-2229 (2011)

Zr-Al alloys containing up to 26 at.% aluminum, prepared by magnetron sputtering, have been anodized in 0.1 mol dm^{-3} ammonium pentaborate electrolyte, and the structure and dielectric properties of the resultant anodic oxide films have been examined by grazing incidence X-ray diffraction, transmission electron microscopy, Rutherford backscattering spectroscopy, and AC impedance spectroscopy. The anodic oxide film formed on zirconium consists of monoclinic and tetragonal ZrO_2 with the former being a major phase. Two-layered anodic oxide films, comprising an outer thin amorphous layer and an inner main layer of crystalline tetragonal ZrO_2 phase, are formed on the Zr-Al alloys containing 5 to 16 at.% aluminum. Further increase in the aluminum content to 26 at.% results in the formation of amorphous oxide layer throughout the thickness. The anodic oxide films become thin with increasing aluminum content, while the relative permittivity of anodic oxide shows a maximum at the aluminum content of 11 at.%. Due to major contribution of permittivity enhancement, the maximum capacitance of the anodic oxide films is obtained on the Zr-11 at.% Al alloy, being 1.7 times than on zirconium at the formation voltage of 100 V.

Pit growth behaviour of aluminium under galvanostatic control

S. Ono and H. Habazaki

Corrosion Science, **53**, 3521-3525 (2011)

The pit growth process on (1 0 0) aluminium under anodic pulse current in a mixed solution of 1 M HCl and 0.1 M H_2SO_4 at 30 ℃ has been evaluated using potential transient measurements and pit size distributions obtained by scanning electron microscopy. Sustained pit growth is observed for all pits during the initial anodic potential rise before reaching a steady-state etch potential, whereas a substantial fraction of the pits passivate at the steady-state etch potential. The pit growth rate during the initial potential rise is 3.4 μm s^{-1}, which is similar to that at the steady-state etch potential. The growth rates of active pits are potential-independent.

Dielectric breakdown and healing of anodic oxide films on aluminium under single pulse anodizing

S.P. Sah, Y. Tatsuno, Y. Aoki and H. Habazaki

Corrosion Science, **53**, 1838-1844 (2011)

Single pulse anodizing of aluminium micro-electrode has been employed to study the behaviour of dielectric breakdown and subsequent oxide formation on aluminium in alkaline silicate and pentaborate electrolytes. Current transients during applying pulse voltage have been measured, and surface has been observed by scanning electron microscopy. Two types of current transients are observed, depending on the electrolyte and applied voltage. There is a good correlation between the current transient behaviour and the shape of discharge channels. In alkaline silicate electrolyte, circular open pores are healed by increasing the pulse width, but such healing is not obvious in pentaborate electrolyte.

Dielectric properties of anodic films on sputter-deposited Ti-Si porous columnar films

M.T. Tanvir, T. Fujii, Y. Aoki, K. Fushimi and H. Habazaki

Applied Surface Science, **257**, 8295-8300 (2011)

For electrolytic capacitor application of the single-phase Ti alloys containing supersaturated silicon, which form anodic oxide films with superior dielectric properties, porous Ti-7 at% Si columnar films, as well as Ti columnar films, have been prepared by oblique angle magnetron sputtering on to aluminum substrate with a concave cell structure to enhance the surface area and hence capacitance. The deposited films of both Ti and Ti-7 at% Si have isolated columnar morphology with each column revealing nanogranular texture. The distances between columns are

~500 nm, corresponding to the cell size of the textured substrate and the gaps between columns are 100-200 nm. When the porous Ti-7 at% Si film is anodized at a constant current density in ammonium pentaborate electrolyte, the growth of a uniform amorphous oxide film continues to ~35 V, while it is limited to less than 6 V on the porous Ti film. The maximum voltage of the growth of uniform amorphous oxide films on the Ti-7 at% Si films is similar for both the flat and porous columnar films, suggesting little influence of surface roughness on the amorphous-to-crystalline transition of growing anodic oxide under the high electric field. Due to the suppression of crystallization to sufficiently high voltages, the anodic oxide films formed on the porous Ti-7 at% Si film shows markedly improved dielectric properties, in comparison with those on the porous Ti film.

Two-step plasma electrolytic oxidation of Ti-15V-3Al-3Cr-3Sn for wear-resistant and adhesive coating

S. Tsunekawa, Y. Aoki and H. Habazaki

Surface and Coatings Technology, **205**, 4732-4740 (2011)

Ti-15V-3Al-3Cr-3Sn (Ti-15-3) is one of the important practical titanium alloys with high cold deformability and high mechanical strength, but its wear resistance is poor. This paper reports the formation of wear-resistant and adhesive ceramic coatings on Ti-15-3 by two-step plasma electrolytic oxidation (PEO). The PEO of Ti-15-3 has been carried out first in alkaline aluminate electrolyte to form a wear-resistant oxide layer and then in acid electrolyte containing both phosphoric acid and sulfuric acid to improve adhesion of the coating. The coating formed in the alkaline aluminate electrolyte is more than 10 [mu]m thick, and highly crystalline. The main phase is Al_2TiO_5. This coating shows high wear resistance, but is not adherent to substrate due to the development of a number of voids and pores in the oxide layer close to the substrate. A new oxide layer with amorphous structure is formed next to the substrate in the subsequent PEO in the acid electrolyte, during which the voids are filled with a new oxide formed in the acid electrolyte, reducing the porosity. As a consequence, the adhesion of the coating is markedly improved without deteriorating the high wear resistance.

Corrosion and passivation behavior of Mg-Zn-Y-Al alloys prepared by cooling rate-controlled solidification

M. Yamasaki, S. Izumi, Y. Kawamura and H. Habazaki

Applied Surface Science, **257**, 8258-8267 (2011)

Highly corrosion-resistant nanocrystalline Mg-Zn-Y-Al multi-phase alloys have been prepared by consolidation of rapidly solidified (RS) ribbons. The relation between corrosion behavior and microstructure evolution of Mg-Zn-Y-Al alloys with a long period stacking ordered phase has been investigated. In order to clarify the influence of rapid solidification on the occurrence of localized corrosion such as filiform corrosion, several $Mg_{96.75}Zn_{0.75}Y_2Al_{0.5}$ (at.%) alloys with different cooling rates are fabricated by the gravity casting, copper mould injection casting and melt-spinning techniques and their corrosion behavior and microstructures are examined by the salt water immersion test, electrochemical measurements, GDOES, XRD, SEM and TEM. To clarify the effect of aluminium addition on the improvement in corrosion resistance of the alloys, several $Mg_{97.25-x}Zn_{0.75}Y_2Al_x$ alloys with different aluminium contents are fabricated by consolidating RS ribbons and the formation of corroded films on the Mg-Zn-Y-Al alloys have been investigated. Rapid solidification brings about the grain refinement and an increase in the solid solubility of zinc, yttrium and aluminium into the magnesium matrix, enhancing microstructural and electrochemical homogeneity, which in turn enhanced corrosion resistance. The addition of aluminium to magnesium can modify the structure and chemical composition of surface films and improves the resistance to local breakdown of the films.

Effect of electrolyte temperature on the formation of self-organized anodic niobium oxide microcones in hot phosphate-glycerol electrolyte

S. Yang, Y. Aoki and H. Habazaki

Applied Surface Science, **257**, 8190-8195 (2011)

Nanoporous niobium oxide films with microcone-type surface morphology were formed by anodizing at 10 V in glycerol electrolyte containing 0.6 mol dm^{-3} K_2HPO_4 and 0.2 mol dm^{-3} K_3PO_4 in a temperature range of 428-453 K. The microcones appeared after prolonged anodizing, but the required time was largely reduced by increasing electrolyte temperature. The anodic oxide was initially amorphous at all temperatures, but crystalline oxide nucleated during anodizing. The anodic oxide microcones, which were crystalline, appeared on surface as a consequence of preferential chemical dissolution of initially formed amorphous oxide. The chemical dissolution of an initially formed amorphous layer was accelerated by increasing the electrolyte temperature, with negligible influence of the temperature on the morphology of microcones up to 448 K.

Growth of porous anodic alumina films in hot phosphate–glycerol electrolyte

S. Yang, Y. Aoki, P. Skeldon, G. Thompson and H. Habazaki

Journal of Solid State Electrochemistry, **15**, 689-696 (2011)

Growth of porous anodic alumina films has been examined at 10 V in hot phosphate-containing glycerol electrolyte containing 0.1 to 0.57 mass% water. The growth rate of the films is highly dependent upon the water content of the electrolyte, reducing markedly at a water content of 0.1 mass%, an opposite trend to that found previously for the formation of porous films on titanium and niobium. Chemical dissolution of the anodic alumina is also suppressed in electrolyte of low water content. GDOES depth profiles revealed that an increased water content of the electrolyte promoted the incorporation of phosphorus species into the films, although chemical dissolution reduced the amounts of phosphorus in the outer regions. Carbon species also appeared to be present in films, particularly at lower water content. Using a niobium oxide outer layer to suppress chemical dissolution resulted in films that were about 1.2 times the thickness of the consumed aluminium for an electrolyte containing 0.25 mass% water. The expansion suggests a possible contribution of field-assisted flow of film material in the growth of the porous anodic film.

Control of morphology and surface wettability of anodic niobium oxide microcones formed in hot phosphate-glycerol electrolytes

S. Yang, H. Habazaki, T. Fujii, Y. Aoki, P. Skeldon and G.E. Thompson

Electrochimica Acta, **56**, 7446-7453 (2011)

We report the fabrication of superhydrophobic surfaces with a hierarchical morphology by self-organized anodizing process. Simply by anodizing of niobium metal in hot phosphate-glycerol electrolyte, niobium oxide microcones, consisting of highly branched oxide nanofibers, develop on the surface. The size of the microcones and their tip angles are controlled by changing the applied potential difference in anodizing and the water content in the electrolyte. Reduction of the water content increases the size of the microcones, with the nanofibers changing to nanoparticles. The size of microcones is also reduced by increasing the applied potential difference, without influencing the tip angle. The hierarchical oxide surfaces are superhydrophilic, with static contact angles close to 0°. Coating of the anodic oxide films with a

monolayer of fluoroalkyl phosphate makes the surfaces superhydrophobic with a contact angle for water as high as 175° and a very small contact angle hysteresis of only 2°. The present results indicate that the larger microcones with smaller tip angles show the higher contact angle for water.

Improved thermal stability of efficient proton-conducting anodic ZrO_2-WO_3 nanofilms by incorporation of silicon species

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

Journal of the Electrochemical Society, **158**, C385-C390 (2011)

Novel proton-conducting amorphous anodic ZrO_2-WO_3-SiO_2 films, 200 nm thick, are prepared by anodizing of sputter-deposited $Zr_{37}W_{47}Si_{16}$ at 100 V with current decay for 1.8 ks in 0.1 mol dm^{-3} phosphoric acid electrolyte at 20°C. The resultant anodic films have been characterized using electrochemical impedance spectroscopy, transmission electron microscopy, glow discharge optical emission spectroscopy and Rutherford backscattering spectroscopy. The addition of silicon species to the anodic ZrO_2-WO_3 film significantly enhanced the thermal stability. Even after thermal treatment at 300°C in dry Ar atmosphere, the anodic ZrO_2-WO_3-SiO_2 films revealed stable proton conductivity in the temperature range of 50–225°C, while the anodic ZrO_2-WO_3 on the $Zr_{43}W_{57}$ loses the proton conductivity by annealing at 250°C. The anodic film on the $Zr_{37}W_{47}Si_{16}$ consisted of two layers, comprising an outer thin ZrO_2 layer, free from tungsten and silicon species, and an inner main layer containing all zirconium, tungsten and silicon species. The results in this study suggest that the conductivity deterioration at high annealing temperatures is associated with the diffusion-induced formation of a poorly-conducting layer near the alloy/anodic oxide interface.

Volume expansion factor and growth efficiency of anodic alumina formed in sulphuric acid

F. Zhou, A.K.M. Al-Zenati, A. Baron-Wiechec, M. Curioni, S.J. Garcia-Vergara, H. Habazaki, P. Skeldon and G.E. Thompson

Journal of the Electrochemical Society, **158**, C202-C214 (2011)

The growth of anodic alumina in sulphuric acid is investigated at constant current on

bulk and sputtering-deposited aluminium. The ratio of the thickness of the film to the thickness of oxidized aluminium is shown to increase with increase of the current density (from 0.5 to 50 mA cm^{-2}) and with decrease of the electrolyte temperature (from 20 to 0 degrees C). In addition, the sulphur content of the films and the efficiency of film formation increase. It is suggested that pores are generated primarily by dissolution at current densities below similar to 2 mA cm^{-2}, with flow of film material dominating at higher current densities.

Failure Characteristics of Scales Formed on Si-Containing Low Carbon Steels during Cooling - Influences of Cooling Rate and Water Vapor

H.Nakata, A. Yamauchi, S. Taniguchi, I-R. Shon, J-W. Choi and K. Kurokawa

Materials Science Forum, **696**, 101-106 (2011)

Low carbon steels containing Si of 0.1 and 1.0 mass%, and 99.5 mass% pure Fe were oxidized in laboratory air and in a H_2O-containing atmosphere at 1173 K. Acoustic emission technique was used to assess the temperature (T_F) at which the first major scale failure takes place during cooling. TF of 1.0 %Si steel oxidized in the air was found to increase with an increase in the scale thickness and cooling rate, while T_F of 0.1 %Si steel had almost no dependence on these parameters. Moreover, the values of T_F of both the steels oxidized in the H_2O-containing atmosphere are higher than those in the air. These differences are attributable to the cooling rate, scale structure, and eutectoid reaction. In general, higher cooling rate implies a higher strain rate and there may be a larger temperature gradient across the scale thickness, which additionally enhances the scale failure. The metallographic examinations revealed that eutectoid magnetite particles in the scales formed on 0.1 %Si steel coarsen as the cooling rate decreases and magnetite seam was formed at the bottom of the iron oxide layer. It is clear that the influence of magnetite precipitation increases as the cooling rate decreases and thus the stress in the scale increases.

Oxidation Behavior of β-SiAlON in H_2O-Containing Atmosphere

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

Materials Science Forum, **696**, 395-399 (2011)

The oxidation behavior of β-SiAlONs ($Si_{6-z}Al_zO_zN_{8-z}$, z = 1, 3, and 4) was investigated at temperature ranging from 1473 to 1673 K in a (N_2-3%O_2)-20%H_2O atmosphere. Oxidation kinetics was followed on the basis of the mass gains, and the oxidized specimens were characterized by FE-SEM, XRD, and EPMA. The mass gain was found to clearly increase with temperature and the z value. For oxidation at 1473 and 1573 K, the gain in mass was observed to be small. During oxidation at 1573 K, mass loss occurred. This loss may be because of the formation of volatile $SiO(OH)_2$. The changes in mass depended on the z value. On the other hand, the oxidation rates at 1673 K were found to be higher than those at and below 1573 K by more than one order of magnitude. The oxidation kinetics at 1673 K followed an almost linear rate law. The XRD and EPMA results showed that the oxide formed on β-SiAlON (z = 1) was composed of a mixture of amorphous aluminosilicate and mullite, whereas that on β-SiAlONs (z = 3 and 4) was composed only of mullite.

Tie-Lined Compositions of the γ and δ Phases in the Binary Re-Ni System

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

J. Japan Inst. Metals, **75**, 479-484 (2011)

Compositions with tie-lines between the γ and δ phases in a binary Re-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 heating times were observed and their concentration profiles for Re and Ni were measured using an electron probe micro-analyzer (EPMA). The Re-40 at% Ni alloy consisted of the γ and δ phases. The tie-lined compositions of the γ and δ phases are summarized as follows (in at%); γ: 13.4Re-86.6Ni, δ: 71.7Re-28.3Ni at 1423 K, γ: 16.4Re-83.6Ni, δ: 69.3Re-30.7Ni at 1573 K, γ: 20.2Re-79.8Ni, δ: 65.3Re-34.7Ni at 1773 K. The Re-Ni alloy powder sintered using the Spark Plasma Sintering (SPS) method were investigated. Solubility limit of Ni in the δ phase in the binary alloy system at 1423 K was found to be 28.3 at% Ni.

Tie-Line Compositions of the σ and (γ, δ) Phases in the Re-Cr-Ni System at 1573 K

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

Materials Transactions, **52** , 2174-2177 (2011)

Compositions with tie lines between the σ and (γ, δ) phases in a ternary Re-Cr-Ni system were investigated by heat treating various ternary Re-Cr-Ni alloys at 1573 K in vacuum for up to 2000 h. The microstructures of the Re-containing alloys that had been water quenched after various heat treatment for times were observed and their concentration profiles for Re, Cr, and Ni were measured using an electron probe microanalyzer. The Re-Cr-Ni alloys consisted of the σ phase with either the γ or δ phase. The concentration profiles of the γ phase became flat after short heat treatment, whereas longer times of up to 2000 h were required to achieve the same effect for the σ and δ phases. The tie-line composition (at%) of each phase at 1573 K was experimentally determined as follows. The σ phase tie-line with the γ phase (17.3 Re, 20.6 Cr, and 62.1 Ni) consists of 53.1 Re, 25.5 Cr, and 21.4 Ni. The σ phase tie-lined with the γ phase (16.9 Re, 19.2 Cr, and 63.9 Ni) consists of 53.0 Re, 24.6 Cr, and 22.4 Ni. The σ phase tie-line with the γ phase (12.7 Re, 24.8 Cr, and 62.5 Ni) consists of 48.4 Re, 30.9 Cr, and 20.7 Ni. The σ phase tie-line with the γ phase (6.1 Re, 46.2 Cr, and 47.7 Ni) consists of 28.1 Re, 52.3 Cr, and 19.6 Ni. The σ phase tie-line with the δ phase (85.6 Re, 5.2 Cr, and 9.2 Ni) consists of 61.1 Re, 27.7 Cr, and 11.2 Ni.

High Temperature Corrosion of CoNiCrAlY-Si Alloys in an Air-Na_2SO_4-NaCl Gas Atmosphere

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

Materials Transactions, **52** , 433-438 (2011)

The addition of Si to CoNiCrAlY was considered in order to develop corrosion resistant alloys for coating applications. The high temperature corrosion behavior of spark plasma sintered CoNiCrAlY alloys of 0, 10, 20, and 30 mass% Si content was investigated in an air-(Na_2SO_4+25.7 mass% NaCl) gas atmosphere at elevated temperatures of 923, 1073, and 1273 K. The results showed that CoNiCrAlY-Si alloys formed mainly an Al_2O_3 or Al_2O_3/SiO_2 scale, depending on the alloy composition and the temperature. The addition of 30 mass% Si significantly improved the high-temperature corrosion resistance of CoNiCrAlY alloy in an air-(Na_2SO_4+25.7 mass% NaCl) gas atmosphere at these temperatures. The high temperature corrosion behavior of CoNiCrAlY-Si alloys was discussed in the present paper.

High Temperature Corrosion Behavior of Si-containing Alloys in the Gas Phase of Air-(Na_2SO_4+25.7mass%NaCl)

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

Materials Science Forum , **696**, 272-277, (2011)

The objective of this study is to develop an excellent corrosion resistant alloy for high temperature coating applications. The Si-containing alloys consisting of CoNiCrAlY and $CrSi_2$ alloys with varying Si and Ni content respectively were prepared by spark plasma sintering (SPS) technique. The corrosion behavior of these alloys was investigated in the gas phase of air-(Na_2SO_4+25.7mass%NaCl) at elevated temperatures of 923, 1073 and 1273K. The results showed that CoNiCrAlY alloy with 30mass% Si content and $CrSi_2$ alloy with 10mass% Ni content were the most effective materials for application in the gas phase of air-(Na_2SO_4+25.7mass%NaCl) due to the formation of protective Al_2O_3/SiO_2 and SiO_2 scale, respectively. Therefore, it is realized that CoNiCrAlY-30mass% Si and $CrSi_2$-10mass% Si coating are very effective for improving of high temperature corrosion resistance of STBA21 steel.

Investigation of Thermal Coatings on Furnace Water Wall in Pulverized Coal Fired Boiler

S. Kyo, M. Nakamori and K. Kurokawa

Corrosion Engineering of Japan, **60**, 138-140 (2011)

In order to improve high-temperature corrosion and wear resistance, water wall tubes being used in pulverized coal firing boiler are spray-coated with Cr_3C_2-NiCr. In this study, the results obtained in observation/analysis of water wall tubes with the coatings after 2-year service were showed. In the furnace side of the water wall tube, elephant skin-like corrosion, namely local and internal attack of substrate by sulfur and oxygen, was observed. Overlay coating for suppression of the elephant skin-like corrosion was not so effective. (in Japanese)

The Sintering Kinetics of Ultrafine Tungsten Carbide Powders

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

Ceramic International, **37**, 2643-2654 (2011)

The sintering kinetics of nano grained tungsten carbide (*n*-WC) powders has been analyzed by non isothermal and isothermal sintering. Non isothermal sintering experiments reveal a multi staged sintering process in which at least three major sub-stages can be distinguished. The isothermal shrinkage strain also exhibits an asymptotic behavior with time indicating an end point density phenomenon in most of the temperature ranges. Combined microstructural and kinetic data analyses suggest that differences in the sinterability of inter and intra agglomerate pore phases introduce sub-stages in the sintering process which manifest as stagnant density regions in both the isothermal and non isothermal experiments. Kinetic analysis of the data reveals very low activation energies for sintering suggesting that particle rearrangement and agglomeration at low temperatures may be brought about by surface diffusion leading to neck growth and grain rotation. At higher temperatures rapid grain boundary diffusion by overheating along inter particle boundaries induced by sparking may be a dominant sintering mechanism. Although grain growth and densification in conventional WC powders generally obey an inverse relation to each other, in *n*-WC powders both can act synergistically to increase the net densification rate. In fact, complete densification cannot be achieved in *n*-WC powders without grain growth as one abets the other.

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.

Observation of 3D network nano-structure of Carbon Nanotubes Scaffold for cultivation

S. Abe, K. Ishikawa, A. Hyono, H. Kobayashi, T. Kiba, T. Akasaka, M. Uo, Y. Yawaka, S.-I. Sato, T. Yonezwa, and F. Watari

J. Surface Science and Nanotechnology **9**, 80-84 (2011)

Development of scaffolds consisting of micro-/nano-sized materials have attracted a great deal of attention for their potential use in tissue engineering tools. We prepared a cell culture scaffold of carbon nanotubes, which is a typical bio-inert nanomaterial, and then investigated the surface morphology and properties. A three-dimensional nano-level network structure was observed using a scanning electron microscope and an atomic force microscope. The scaffold also exhibited excellent protein absorption. In order to apply the obtained scaffold to the cultivation of osteoblast cells, the cytocompatibility was comparable to that of a conventional cell culture dish.

Evaporation Processes of Water Molecules from Graphene Edge: DFT and MD Study

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

Computational Materials Science. **50**, 2640-43 (2011)

The evaporation processes of water molecules adsorbed in the edge region of graphene have been investigated by means of direct MO–MD method. A large system composed of 29 water molecules and a graphene sheet (C96H24) was used as a model system. The edge carbon atom of graphene was terminated by hydrogen atom. The geometry optimization showed that the water molecules interact with the hydrogen atoms in the edge region of graphene. At low temperature (300 K), the water molecules were dissociated as water clusters from the graphene. On the other hand, in addition to the dissociation of water clusters, the isolated water molecule was also found as dissociation product at high temperature (500 K). The mechanism of water evaporation was discussed on the basis of theoretical results.

The interaction between carbon nanomaterials and polypeptide: An in vitro and in silico study

S. Abe, R. Komine, Y. Nagoya, F. Watari, and H. Tachikawa

Molecular Crystals and Liquid Crystals., **538**, 258-264 (2011)

The interaction of carbon nanotubes (CNTs) and peptide molecule has been investigated by means of experiment and theoretical calculations. For comparison, the graphene-peptide system was investigated with the same manner. It was found that peptide interacts strongly with the CNTs, whereas the interaction of graphene with the peptide is negligibly small. The theoretical calculation supports strongly these findings.

Internal Distribution of Micro-/Nano-sized Inorganic Particles and their Cytocompatibility

S. Abe, N. Iwadera, M. Esaki, I. Kida, M. Mutoh, T. Akasaka, M. Uo, Y. Yawaka, M. Morita, K Haneda, T. Yonezawa, and F, Watari

Mater. Sci. Eng., **18**, 19201301-04 (2011)

Nano-sized materials have received much attention lately, both in terms of their multiple applications and their biocompatibility. From both viewpoints, understanding the biodistribution of administered nano-materials is very important. In this study, we succeeded in visualizing the biodistribution of administered nano-materials using a scanning X-ray analytical microscope and magnetic resonance imaging method. Quantitative observation was carried out by inductively coupled plasma - atomic emission spectroscopy. We observed that the administered nano-particles accumulated in the liver, lung and spleen of mice. To estimate their cytocompatibility, the nano-particles were exposed to human liver cells. The results suggested that the micro-/ nano- particles have good cytocompatibility, except for copper oxide nano-particles.

Versatile surface modification by carbon nanotubes through an amide-bond formation

S. Abe, K. Nakayama, H. Kobayashi, T. Kiba, T. Akasaka, S.-I. Sato, M. Uo, F. Watari, and T. Takada

Nano Biomedicine, **3**, 208-216 (2011)

Nano-sized materials have received much attention lately, both in terms of their multiple applications and their biocompatibility. From both viewpoints, understanding the biodistribution of administered nano-materials is very important. In this study, we succeeded in visualizing the biodistribution of administered nano-materials using a scanning X-ray analytical microscope and magnetic resonance imaging method. Quantitative observation was carried out by inductively coupled plasma - atomic emission spectroscopy. We observed that the administered nano-particles accumulated in the liver, lung and spleen of mice. To estimate their cytocompatibility, the nano-particles were exposed to human liver cells. The results suggested that the micro-/ nano- particles have good cytocompatibility, except for copper oxide nano-particles.

Density Functional Theory (DFT) Study on the water clusters on Graphene Chip

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

Jpn. J. Appl. Phys., **50**, 01BJ0201-03 (2011)

The structures and electronic states of graphene–water interaction systems have been investigated by means of density functional theory (DFT) method to elucidate the effects of water clusters on the electronic states of graphene chip. Solvation caused by five to eight water molecules (n = 5–8) was examined as the interaction systems. A graphene chip composed of 14 benzene rings was used as a model of finite-sized graphene (C42H16). The water clusters interact with the graphene chip with hydrogen bonds. The band gap of graphene was slightly red-shifted by the solvation and the first excitation energy was saturated around n = 5. The electronic states of graphene–water systems were discussed on the basis of theoretical results.

Development of a novel transparent substrate coated by carbon nanotubes through covalent bonding

S. Abe, K Nakayama, D. Hayashi, T. Akasaka, M. Uo, F. Watari and T. Takada

Physics Procedia, **14**, 147-151 (2011)

There is considerable investigation into the applications of carbon nanotubes because of their valuable properties. In this study, we succeeded in poly-carboxylation of multi-walled carbon nanotubes (CNTs) tethered to a glass substrate through covalent bonding. By causing a carboxylation reaction using a peroxide derivative, we were able to observe many carboxyl groups on the surfaces of CNTs. We characterized the obtained CNTs derivatives using Infrared and Raman spectroscopy. The CNTs reacted directly with glass substrates that presented amino groups, and the tethered CNTs were not removed from the substrate by sonication, suggesting the formation of a strong bond between the CNTs and substrate. Nanostructures in the shape of curled individual strings were observed using a scanning electron microscope and an atomic force microscope. The transparency of substrates was more than 97% in visible regions.

Biodistribution and Biocompatibility of poly(lactic acid)-coated SiO_2 particles

S. Abe, A. Sasaki, N. Iwadera, T. Akasaka, M. Uo, and F. Watari

Nano Biomedicine, **3**, 300-305 (2011)

Nano-sized materials have received much attention lately, both in terms of their multiple applications and their biocompatibility. From both viewpoints, understanding the biodistribution of administered nano-materials is very important. In this study, we succeeded in visualizing the biodistribution of administered nano-materials using a scanning X-ray analytical microscope and magnetic resonance imaging method. Quantitative observation was carried out by inductively coupled plasma - atomic emission spectroscopy. We observed that the administered nano-particles accumulated in the liver, lung and spleen of mice. To estimate their cytocompatibility, the nano-particles were exposed to human liver cells. The results suggested that the micro-/ nano- particles have good cytocompatibility, except for copper oxide nano-particles.

Reverse phase transformation from α to γ in 9Cr-ODS ferritic steels

M. Yamamoto, S. Ukai, S. Hayashi, T. Kaito and S. Ohtsuka

Journal of Nuclear Materials **417**, 237–240 (2011)

The process of residual ferrite formation and resultant high-temperature strengthening in 9Cr-ODS ferritic steel was investigated by TEM observation, dilatometric measurement and thermodynamic analysis. Formation of the residual ferrite is dominated by a balance between pinning of α–γ interfaces and theα–γ reverse transformation, andα–γ reverse transformation is affected by dissolution of carbides into the c-matrix at the AC1 and AC3 points. The fine size of oxide particles is responsible for the higher strength of the residual ferrite containing ODS steels.

High-strength of modified Ausform 9CrODS steels

S. Ukai, M. Yamamoto, N. Chikada, S. Hayashi, T. Kaito, S. Ohtsuka, T. Azuma and S. Ohsaki

Journal of Nuclear Materials **417**, 154–157 (2011)

Hot-rolling at the austenitic c phase (1000°C) led to a formation of ultra-fine grains and a high dislocation density within grain interiors by an Ausform process. Those heavily accumulated strains accelerated coarsening of prior austenite grains, and block grains transformed from the coarsened prior austenite grains were also coarser in the subsequent normalizing heat treatment. This process is called as modified Ausform process. The modified Ausform 9CrODS steels were improved in the ultimate tensile strength at 700 °C due to the formation of uniformly coarser block grains.

γ' Precipitation and Growth Kinetics in Mechanically Alloyed Ni–Al

Q. X. Tang, S. Ukai, A. Minami and Shigenari Hayashi

Advances in Materials Science and Engineering, 7, (2011)

The precipitation and growth kinetics of *γ'* precipitates, which are strengthening factors in Ni-base oxide dispersion strengthened (ODS) superalloys, were investigated. The cuboidal-type *γ'* precipitates are formed in conventional arc-melted Ni–Al alloys, whereas spherical-type precipitates are formed in the mechanically alloyed (MAed) specimens. The morphology is controlled by a latticemisfit between the *γ'* precipitates and the matrix at the aging temperature of 800□C. The growth kinetics of the *γ'* precipitates can be followed by Ostwald ripening. The Arrhenius plot yielded a lower

activation energy for the solute atom diffusion in MAed specimens, which is attributed to their high dislocation density and nanosized grains.

Microstructure Control of Co-base ODS alloys

K. Takezawa, S. Ukai and S. Hayashi

Advanced Materials Research **239-242**, 864-867 (2011)

As high-temperature metallic materials, Co-base ODS alloys were produced by means of mechanical alloying, spark plasma sintering and hot rolling. Co-3wt%Al-1.2wt%Hf-ODS alloy was found to be an attractive composite like material, which is formed by spinodal like decomposition. The metastable phases were traced by hard phase containing dense oxide particles and soft one containing less oxide particles. Their tensile stress at 1,000 ºC was improved by Hf addition that forms Y2Hf2O7 type oxide particles and shortens their space distance.

Grain Boundary Deformation at High Temperature Tensile Tests in ODS Ferritic Steel

Y. Sugino, S. Ukai, B. Leng, Q. X. Tagng, S. Hayashi, T. Kaito and S. Ohtsuka

ISIJ International, **51**, 982-986 (2011)

The tensile test of the recrystallized ODS ferritic steels was performed in the loading direction for the longitudinal and 45° inclined with respect to the grains alignment. The testing temperature was 800°C and the strain rate was 10–4 s–1. A clear serration structure was observed at near the grain boundaries at the surface of 45° specimen ruptured. This is a clear evidence of the occurrence of the grain boundary sliding in 45° direction. For the total strain of 12% in 45° direction, grain boundary deformation induced by sliding was estimated about 9%, whereas the amounts of the transgranular strains was 2% measured by EBSD analysis. The grain-subdivision was also identified near grain boundaries by FIB analysis, which could be caused by a dynamic recrystallization during the localized grain boundary deformation.

Directional recrystallization of ODS alloys by means of zone annealing

Y. Sugino, S. Ukai, S. Hayashi, Q. X. Tang and B. Leng

Journal of Nuclear Materials **417**, 171–175 (2011)

A process of the directional recrystallization in Fe-base ODS ferrite, nickel and Ni-based ODS alloy was investigated by using a zone annealing equipment. Zone annealing promotes the formation of the recrystallized grains for Ni and Ni-base ODS alloy. For Fe-base ODS ferrite, the zone annealing is not effective and the directional recrystallization is mainly affected by the cold-rolled structure. The effective pinning by the dispersed yttria particles against grain boundary movement was also verified.

Transient liquid-phase bonding of ODS steels

H. Noto, S. Ukai and S. Hayashi

Journal of Nuclear Materials **417**, 249–252 (2011)

The use of transient liquid-phase bonding of 9CrODS steels using Fe–3B–2Si–0.5C filler was investigated for bonding temperature of 1180ºC and hold times of 0.5–4.0 h. The sequential process, consisting of isothermal melting, solidification and homogenization, was confirmed for bonding the 9CrODS steel. The precipitation of chromium boride found in 19CrODS steel is avoided in 9CrODS steel due to the lower Cr content. Silicon tends to be slightly enriched inside the bonding zone. Agglomeration and coarsening of Y_2O_3 particles in 9CrODS steel lead to softening inside the bonding zone formed by incipient melting of the foil bonding alloy, and in a diffusion affected zone (DAZ) adjacent to the bonding zone.

Effect of tungsten addition on microstructure and high temperature strength of 9CrODS ferritic steel

T. Narita, S. Ukai, S. Ohtsuka and M. Inoue

Journal of Nuclear Materials, **417**, 158–161 (2011)

Tungsten is an effective element for solid-solution strengthening and is a ferrite former in 9CrODS ferritic steel, however excessive tungsten leads to Laves phase

formation. Appropriate tungsten concentration in 9CrODS ferritic steel was found to be around 2 mass%, which produces high temperature strength without Laves phase precipitation. The stress increment due to solid-solution strengthening by tungsten was characterized as relatively small, compared to enhanced ferrite formation, the so called residual α-ferrite.

Recrystallization Texture of Cold-rolled Oxide Dispersion Strengthened Ferritic Steel

B. Leng. S. Ukai, Y. Sugino, Q. X. Tang, T. Narita, S. Hayashi, F. Wang, S. Ohtsuka and T. Kaito

ISIJ International, **51**, 951–957 (2011)

The recrystallization behavior of a 88% cold-rolled 15Cr–ODS ferritic steel was investigated. Specimens annealed at low and high temperatures show two different recrystallization modes. Annealing at 1 000°C generates a structure consisting of coarse grains with {110}<112> texture, while annealing at 1 150°C and 1 300°C produce fine grains with {111}<112> texture. This phenomenon is ascribed to that the mobility of boundaries between {110}<112> nuclei and {001}<110> deformed matrix are higher than between {111}<112> nuclei and {001}<110> deformed matrix. Also it is found that a recovery annealing at 900°C prior to recrystallization annealing will retard recrystallization, which results in a structure of coarse grains with {110}<112> texture even after the following annealing at 1 300°C.

Grain characteristic and texture evolution in friction stir welds of nanostructured oxide dispersion strengthened ferritic steel

W. T. Han, F. R. Wan, B. Leng, S. Ukai, Q. X. Tang, S. Hayashi, J. C. He1 and Y. Sugino

Science and Technology of Welding and Joining, **16**, 690-696 (2011)

The present paper investigated the grain and texture characteristics in a nanostructured oxide dispersion strengthened ferritic steel subjected to friction stir welding. The ‘onion rings’ structure obviously exhibited in the macrostructure overview of the welds. The electron backscatter diffraction (EBSD) work revealed that the ‘onion rings’ comprised alternate layers made by coarse and fine grains, while

no strong texture was exhibited in the alternate layers of the 'onion rings'. Image quality maps of EBSD indicated that layers of fine grains were deformed under high strain conditions. Textures within the stir zone and thermomechanically affected zone were weak and exhibited some characteristics of bcc simple shear textures. Results of grain boundary revealed that the mechanical action in welding process promoted the transformation of low angle to high angle boundaries and contributed to the grain refinement.

Development of Al added high-Cr ODS steels for fuel cladding of next generation nuclear systems

A. Kimura, R. Kasada, N. Iwata, H. Kishimoto, C.H. Zhang, J. Isselin, P. Dou, J.H. Lee, N. Muthukumar, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe

Journal of Nuclear Materials, **417**, 176–179 (2011)

A successful example of high-Cr oxide dispersion strengthened (ODS) steels development is introduced with showing key technologies to overcome the issues to meet material requirements for next generation nuclear systems as well as fusion blanket systems. Corrosion issue requires Cr concentration more than 14 wt.%, but aging embrittlement issue requires it less than 16 wt.%. An addition of 4 wt.% Al is effective to improve corrosion resistance of 16 wt.% Cr-ODS steel in supercritical water (SCW) and lead–bismuth eutectics (LBE), while it is detrimental to high-temperature strength. An addition of small amount of Zr or Hf results in a significant increase in creep strength at 973 K in Al-added ODS steels. Feasibility of high-Cr ODS steel without Al addition is assessed for fusion application in terms of corrosion resistance in SCW.

Anisotropy in tensile and ductile–brittle transition behavior of ODS ferritic steels

R. Kasada, S.G. Lee, J. Isselin, J.H. Lee, T. Omura, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe

Journal of Nuclear Materials, **417**, 180–184 (2011)

Anisotropic fracture behavior of SOC-1 oxide dispersion strengthened (ODS) ferritic steel has been investigated for a hot-extruded bar by tensile tests and Charpy impact

tests. These mechanical properties are better in the longitudinal direction than in the transverse directions against extrusion direction (ED). Fracture surface observations by scanning electron microscopy and auger electron spectroscopy indicated bundle-like morphology with existence of segregation/precipitation/inclusions along ED. Pole figures of the hot-extruded bar characterized using electron back scattering diffraction (EBSD) technique and Xray diffraction exhibited h1 1 0i fiber texture formation along ED. The EBSD orientation map showed a complex bundle-like grain morphology which consists of elongated grains having a specific orientation h1 1 0i// ED and relatively isotropic and small grains having other orientation. The results conclude that the combined effects of observed elongated grain morphology and these small grains with segregation/ precipitation/inclusions along ED can explain the anisotropic fracture behavior of the hot-extruded ODS ferritic steel.

Effects of MA environment on the mechanical and microstructural properties of ODS ferritic steels

N. Y. Iwata, T. Liu, P. Dou, R. Kasada, A. Kimura, T. Okuda, M. Inoue, F. Abe, S. Ukai, S. Ohnuki and T. Fujisawa

Journal of Nuclear Materials, **417**, 162–165 (2011)

The mechanical and microstructural properties of ODS ferritic steels mechanically alloyed (MA) in different atmospheres were investigated. Milling in the presence of nitrogen gas significantly reduced the particle size of the Fe–15.5Cr–2W–4Al–1Zr–0.35Y2O3 powder. After solidification of the MA powder, no bubble formation was found in the matrix of the steel mechanically alloyed in hydrogen atmosphere. A slight deterioration in the impact properties was attributed to the formation of large Zr(C,N) precipitates, as observed both in grains and on grain boundaries by TEM.

Evaluation of fracture behavior of recrystallized and aged high-Cr ODS ferritic steels

J. Isselin, R. Kasada, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe

Journal of Nuclear Materials, **417**, 185–188 (2011)

The effect of aging on the ductile to brittle transition behavior of recrystallized

high-Cr ODS ferritic steels were investigated using small-punch test technique. In order to reduce the anisotropy of microstructure in the as-received ODS steels, they were recrystallized after cold rolling. The ODS steel without Al hardly recrystallized at 1200 ºC for 90 min, while the ODS steel with Al significantly recrystallized. Ductile– brittle transition curves were drawn for as received, recrystallized, and thermally aged (at 450 ºC for 1440 h). Before aging, both materials had good impact properties with low ductile–brittle transition temperatures and high USEs. The ductile–brittle transition temperatures are not dependent of the grain size. The aging degraded their impact properties for ODS steel with Al. However, almost no degradation occurred for the ODS steel without Al. SEM observation showed an influence of the cold-rolling direction on the fracture behavior especially at low temperatures.

Polymorphic and coherency transition of Y–Al complex oxide particles with extrusion temperature in an Al-alloyed high-Cr oxide dispersion strengthened ferritic steel

P. Dou, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe

Acta Materialia, **59**, 992–1002 (2011)

The phase and metal/oxide interface structure of the nanometer-scale particles in an Al-alloyed high-Cr oxide dispersion strengthened ferritic steel extruded at 1150 ºC and 1050 ºC were characterized by high-resolution transmission electron microscopy and diffraction contrast techniques, including weak beam electron microscopy. After extrusion at 1150 ºC, yttrium–aluminum–hexagonal (YAH, YAlO3) and yttrium–aluminum–perovskite (YAP, YAlO3) oxides (diameter610 nm) constitute_55% and 38% of the particles, respectively; _78% of the particles (4.5–10 nm in diameter), which include 40%YAHoxide and 38% YAP phase with misfit (translational) moire´ fringe spacing of 2.15 nm and 1.65 nm, respectively, are semi-coherent with the matrix. After extrusion at 1050 ºC, almost all the particles are YAH phase, and _86.5% (diameter <4.5 nm) are coherent with the matrix. The coherency of the oxides is size dependent. The crystallographic orientation correlations of the oxides and matrix were found.

Effects of extrusion temperature on the nano-mesoscopic structure and mechanical properties of an Al-alloyed high-Cr ODS ferritic steel

P. Dou , A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa and F. Abe

Journal of Nuclear Materials, **417**, 166–170 (2011)

The nano-mesoscopic structure of a newly developed Al-alloyed high-Cr oxide-dispersion-strengthened (ODS) ferritic steel, which was extruded at 1150 and 1050 ºC, has been characterized by transmission electron microscopy to correlate with microhardness at room temperature. The grain size decreases, the number density of the oxide particles increases and their size decreases, and the microhardness increases, with decreasing extrusion temperature. After extrusion at 1150 ºC, most of the oxide particles in the ODS steel are semi-coherent (78%). The semi-coherent particles were divided into two types with almost equal fraction according to the spacings of surrounding misfit moire fringes, which are about 2 nm and 1.65 nm, indicating the misfit strains to be 0.075 and 0.092, respectively. After 1050 ºC extrusion, most of the oxide particles are coherent (86%). The misfit strains of the coherent particles and a few semi-coherent particles are about 0.035 and 0.075, respectively. The strengthening mechanism is briefly discussed.

High-temperature carburization behavior of HASTELLOY Y in CH_4 gas

C. Matsukawa, S. Hayashi, H. Yakuwa, T. Kishikawa, T. Narita and S. Ukai

Corrosion Science, **53**, 3131 (2011)

Ni-base wrought alloy HASTELLOY X tube was exposed to Ar–CH_4 at 800 and 1000 _C in order to understand the carburization kinetics of the alloy used for fuel injection nozzles of micro-gas turbine combustors. Three different internal carbides, $(Cr,Mo)_3C_2$, $(Cr,Mo)_7C_3$ and $(Cr,Mo)_{23}C_6$ were observed in this order from the surface, and the partial damage to the outer surface of the specimen tube appeared similar to metal-dusting. The internal carburization kinetics on both the inner and outer parts of tube followed the parabolic rate law. The carbon permeability in HASTELLOY X was obtained, and was slightly smaller than that of Ni–20%Cr.

In-situ measurement of the phase transformation behavior of Al_2O_3 scale during high-temperature oxidation using synchrotron radiation

S. Hayashi, I. Saeki, Y. Nishiyama, T. Doi, S. Kyo and M. Segawa

Materials Science Forum, **696**, 63 (2011)

Very thin Fe-coatings, ~50nm, were found to suppress metastable Al_2O_3 formation on Fe-50Al and Ni-50Al alloys in our previous study. The authors proposed a mechanism whereby α- Al_2O_3 precipitates from the Al-saturated Fe2O3, which was formed during initial oxidation, since α-Al_2O_3 and α-Fe_2O_3 have isomorphous structures. In order to confirm the proposed mechanism, in-situ measurements were made of structural changes in the oxide scales formed on FeAl with and without Fe coating during heating and subsequent isothermal high temperature oxidation by synchrotron radiation with a two-dimensional X-ray detector. Diffraction peaks from Fe_2O_3 were initially observed at around 350°C on Fe-coated samples. The lattice parameter of the Fe_2O_3 initially increased linearly due to thermal expansion, but then rapidly decreased due to the formation of a solid solution of Fe_2O_3-Al_2O_3. α-Al_2O_3 started to appear at around 800°C, but no peaks from metastable Al_2O_3 were observed. The diffraction peaks from the α-Al_2O_3 on Fe-coated samples consisted of two distinct peaks, indicating that the α-Al_2O_3 had two different lattice parameters. These results suggest that the α- Al_2O_3 was formed not only by precipitation from the Al-saturated Fe_2O_3, but also by oxidation of Al in the substrate.

Evolution of Al_2O_3 scale formed on Ni-Al-Pt alloys in atmospheres containing water vapor

M. Auchi, S. Hayashi, T. Narita, and S. Ukai

Materials Science Forum, **696**, 132 (2011)

High temperature cyclic oxidation behavior of γ'-base Ni-25Al-10Pt (in at.%) alloy was investigated at 1000°C in air with and without 30vol.%H_2O. The oxidation mass gain during the initial stage of oxidation was similar in both atmospheres, but the oxidation rate in air+H_2O was lower in the longer steady-state oxidation stage. Metastable Al_2O_3, which formed during the initial stage of oxidation, transformed completely after about 100hr of oxidation in dry air. The transformation to α-Al_2O_3 also occurred in air+H_2O, but complete transformation to α-Al_2O_3 was not observed during the oxidation time in the present study. θ- Al_2O_3 grains remained for longer on

the α- Al_2O_3 layer in air+H_2O and became significantly coarser with oxidation time. The present results indicate that water vapor delays the metastable to α- Al_2O_3 phase transformation, and decreases the growth rate of α- Al_2O_3.

Calciothermic reduction of NiO by molten salt electrolysis of CaO in $CaCl_2$ melt

Reyna Famila Descallar-Arriesgado, Naoto Kobayashi, Tatsuya Kikuchi and Ryosuke O.Suzuki

Electrochimica Acta, **56**, 8422-8429 (2011)

Metallic nickel powders with low and uniform residual oxygen content were produced from NiO using the molten salt electrolysis of CaO in $CaCl_2$ melt. Suitable amount of CaO for the reduction was in the range of 0.5–3.0 mol% CaO.
The electrical isolation of NiO from both electrodes could produce metallic Ni in $CaCl_2$ melt. Separating the metal oxides from the cathode confirmed the mechanism of calciothermic reduction that the electrolysis of dissolved CaO in $CaCl_2$ melt produces Ca, and that the dissolved Ca in molten $CaCl_2$ successfully reduces NiO to metallic Ni. An average of about 600 ppm oxygen in Ni sample was achieved directly from oxide, when NiO was detached from the cathode. DOI: 10.1016/j.electacta.2011.07.027

Experimental study of a Thermoelectric Generation System

J.Zhu, J.Gao, M.Chen, J.Zhang, Q.Du, L.A.Rosendahl and R.O.Suzuki

J. Electronic Materials, **40**, 744-752 (2011)

A flat wall-like thermoelectric generation system is analyzed for applications in exhaust heat of kilns. The essential performance of the thermoelectric generation system is tested, such as open-circuit voltage, output power, and system conversion efficiency. When heat source insulation is not considered, the system conversion is efficient at hot-side temperatures between 120°C and 150°C. The nonuniformity of heat transfer is found to significantly affect the power-generating ability of the system. System-level simulation using a quasi-one-dimensional numerical model and the experiment was compared. DOI: 10.1007/s11664-011-1536-x

Effect of sulfur on the TTT diagram of $CaO-Al_2O_3$ slag at eutectic composition

Yoshiaki Kashiwaya, Yasuaki Kusada and R.O. Suzuki

ISIJ international, **51**, 1974-1981 (2011)

A flat wall-like thermoelectric generation system is analyzed for applications in exhaust heat of kilns. The essential performance of the thermoelectric generation system is tested, such as open-circuit voltage, output power, and system conversion efficiency. When heat source insulation is not considered, the system conversion is efficient at hot-side temperatures between 120°C and 150°C. The nonuniformity of heat transfer is found to significantly affect the power-generating ability of the system. System-level simulation using a quasi-one-dimensional numerical model and the experiment was compared.

Atmosphere controlled hot thermocouple method and crystallization phenomenon of $CaO-Al_2O_3$ eutectic slag

Yoshiaki Kashiwaya, Yasuaki Kusada and R.O. Suzuki

ISIJ international, **51**, 1967-1973 (2011)

The effect of sulfur and oxygen partial pressure on the crystallization behavior was investigated using hot thermocouple technique. The nose position of TTT diagram of $CaO–Al_2O_3$ eutectic composition under Ar atmosphere was 7 s at 1100C, while that under the controlled Ar gas atmosphere were 7 s at 1150C. The lower oxygen potential and higher SO_2 potential enhanced the crystallization at the temperatures higher than the nose temperature. The monocalcium aluminate (CaO·Al2O3) containing a larger amount of sulfur primarily crystallized in the sulfur added slag.

Computational Simulation of Thermoelectric Generators in Marine Power Plants

Min Chen, Yuto Sasaki and R.O. Suzuki

Materials Transactions, **52**, 1549-1552 (2011)

In thermoelectric generation applications, the two indispensable conditions are the hot

source and the cold source to provide the temperature difference for the generator. Thus, the waste heat recovery from various high temperature gas or steam turbines on ships by thermoelectric generators (TEG) is promising because the ocean naturally plays a role as an infinitely large cold source. Among other options, a pilot study of the applicability of thermoelectric generation to the boiler section of marine power plants is presented through CFD (Computational Fluid Dynamics) modeling. It is found that more than 600 W power may be produced from the waste heat of a 300 kW boiler but without an obvious loss of the system safety.

Fabrication of Micro-Circuit with Aluminum and Its Oxide

T. Kikuchi, S. Fujita, and M. Sakairi

J. Surf. Fin. Soc. Jpn., **62**, 451-455 (2011)

Micro-circuit board made of aluminum and its oxide was fabricated by laser irradiation and anodizing. Aluminum covered with porous type oxide film was irradiated with a pulsed YAG laser to remove linearly the anodic oxide film. The specimen was re-anodized in oxalic and ematal anodizing solution to form anodic oxide film at the laser-irradiated area. Finally, the oxide film formed the first anodizing was removed by mechanical polishing. The aluminum and its oxide with 100 μm width and intervals were formed on the board.

Observation of corrosion behavior of stainless steels in a salt manufacturing plant environment using the multichannel electrode method

A. Naganuma and K. Azumi

Corrosion Science, **53**, 1165–1173 (2011)

Crevice corrosion of four kinds of stainless steel, SUS316L, NAS64, NAS185N and NAS254N, in saturated NaCl solution at temperatures up to 100 °C was investigated using the multichannel electrode method. In this method, a pile of five individual working electrodes (WEs) of stainless steel sheet were embedded in epoxy resin and a small hole penetrating through the five WEs was treated as an artificial crevice. Time transition and distribution of the coupling current between the five WEs were measured as a function of crevice depth, kind of stainless steel, temperature and concentration of dissolved oxygen (DO). Anodic or cathodic coupling current on the

five WEs of SUS316L changed depending on their corroding state. On the other hand, NAS64, NAS185N and NAS254N showed that the WE outside the crevice contributed as a cathode and that WEs inside the crevice contributed as an anode. The coupling current on SUS316L was strongly affected by concentration of DO, while the coupling current on NAS64, NAS185N and NAS254N was not affected by DO, probably due to the establishment of a passive state inside the crevice.

Effect of Copper Pretreatment on the Zincate Process and Subsequent Copper Electrodeposition of AZ31 Magnesium Alloy

J. Tang and K. Azumi

Journal of the Electrochemical Society, **158** [9], D535-D540 (2011)

A small amount of Cu^{2+} ions was added to the activation bath used for pretreatment of the plating process of an AZ31 Mg alloy. In the activation process, a small amount of Cu was deposited at high density on the substrate surface accompanying Mg dissolution (Cu pretreatment). These Cu deposits acted as nucleation seeds for Zn deposition in the following zincate process and provided a uniform and dense Zn layer almost completely covering the substrate. The Cu layer electroplated on this zincated substrate showed considerable improvement in density and uniformity compared with those of the sample without Cu pretreatment. Cross- sectional SEM observation revealed that a less-defective interface between the Cu layer and substrate was obtained for the Cu-pre- pared sample. This structure also contributed to the improvement of adhesion strength. The mechanism of this improvement was investigated using electrochemical measurement and scanning electron microscopy observation with energy dispersive X-ray spectroscopy analysis.

Effect of copper pretreatment on the zincate process and subsequent electroplating of a protective copper/nickel deposit on the AZ91D magnesium alloy

J. Tang and K. Azumi

Electrochimica Acta, **56**, 8776–8782 (2011)

To obtain a durable Ni coating with excellent adhesion strength on an AZ91D Mg alloy, a pretreatment was performed with a small amount of Cu^{2+} ions added to the

activation bath used in the pretreatment prior to the plating process. In the pretreatment activation process, a high density Cu layer was deposited on both the α-phase and β-phase areas of the substrate accompanied with Mg dissolution. The Cu deposit acted as nucleation seeds for the Zn deposition in the following zincate process which provided a uniform and dense Zn layer almost completely covering the substrate. Then a thin Cu layer was electroplated on this zincated substrate as an undercoating for the succeeding electroplating with Ni. Cross-sectional scanning electron microscopy observations showed that the Cu deposited by the pretreatment enabled the deposition of a protective Ni layer with few defects. This structure also contributed to the improvement of adhesion strength and corrosion resistance as compared with the non-Cu added sample.

Influence of zincate pretreatment on adhesion strength of a copper electroplating layer on AZ91 D magnesium alloy

J. Tang and K. Azumi

Surface & Coatings Technology, **205**, 3050–3057 (2011)

Cu was electrodeposited on AZ91 D Mg alloy with zincate pretreatment in an alkaline plating bath, and the effect of zincate pretreatment on adhesion strength of the Cu layer was investigated. Scanning electron microscopy results showed that Zn was mainly deposited on the α-phase surface, and ultrasonic agitation at the initial stage of the zincate pretreatment improved the coverage of the Zn layer even on the β-phase surface, resulting in enhancement of the adhesion strength of the Zn layer and the successive Cu layer to the substrate. Adhesion tests revealed that the plating layer peeled off at the mixed layer of Zn and Cu deposits formed at the interface between the zincated layer and the electrodeposited Cu layer. A smooth Cu surface was obtained in the plating bath containing H_3BO_3.

Optimization of pulsed electrodeposition of aluminum from $AlCl_3$-1-ethyl-3-methylimidazolium chloride ionic liquid

J. Tang and K. Azumi

Electrochimica Acta, **56**, 1130–1137 (2011)

In this study, Al was electrodeposited on a platinum substrate at room temperature from an ionic liquid bath of EMIC containing AlCl3 using potentiostatic polarization

(PP), galvanostatic polarization (GP), monopolar current pulse polarization (MCP) and bipolar current pulse polarization (BCP). Transition of current or potential during galvanostatic or pulse polarization revealed that the initial stage of the deposition process was controlled by a nucleation process depending on the polarization condition. For example, the average size of Al deposits decreased with increasing current density in the case of GP. FE-SEM observation showed that dense and compact Al deposits with a smooth surface were obtained by the current pulse method. Roughness factor evaluated from electrochemical impedance measurement confirmed the smooth surface of these deposits. Adhesion strength of Al deposits was greatly improved using BCP in which an anodic pulse was combined with a cathodic pulse for electrodeposition. In this study, the optimal parameters for BCP were found to be I_C = □16.0 mA cm$^{□2}$, I_A = 1.0 mA cm$^{□2}$, r_C (duty ratio) = 0.5, and f = 2 Hz. The mechanisms of electrodeposition by these three methods are discussed.

Optimization of Silver Mirror Reaction for Silver Coating

Y. Aoki and K. Azumi

Journal of the Surface Finishing Society of Japan, **62** [3], 189-192 (2011)

The surface morphology and mass of a silver coating deposited on a glass substrate using silver mirror coating method were investigated as a function of the bath temperature, the glucose concentration used in the plating bath as a reducing agent, and the coating time necessary to obtain good coating quality. Using the optimum coating conditions of 10.8 ks deposition time and 0.2 °C temperature of the plating bath com- posed of 0.2 mol dm^{-3} $[Ag(NH_3)_2]^+$+0.12 mol dm^{-3} glucose, a smooth and uniform silver coating with ca. 150 nm thickness was obtained. Improved adhesion of the silver coat to the glass substrate was obtained by application of an etching pretreatment to the glass substrate using various etchants. A commercially available etchant containing $(NH_4)HF_2$ provides an especially strong anchor effect because it induces a considerably rough dissolution trace to the glass substrate. (Japanese)

Corrosion control in the coating process of Mg alloys

K. Azumi, H. H. Elsentriecy and J. Tang

Journal of the Surface Finishing Society of Japan, **62** [12], 696-701 (2011)

Pickling, zincate, chemical conversion, and electroplating processes were examined

and optimized to obtain highly corrosion-protective coatings on AZ91D and AZ31 Mg alloys based on aspects of corrosion control in respective processes. The Pickling process bath composition was adjusted to suppress pitting corrosion and galvanic coupling corrosion between the α-phase and the β-phase to produce a flat dissolution surface. Potentiostatic anodic polarization was applied in the stannate chemical conversion process to an alloy specimen immersed in the conversion bath, thereby supplying sufficient Mg^{2+} ions to induce formation of a dense and uniform conversion coating. With the zincate process, Cu pretreatment in the precursory activation process enabled dense and uniform Zn deposition suitable for the plating process. Using these methods and conditions, better corrosion-protective coatings with dense, uniform, low-defective and high-adhesive properties were obtained on Mg alloys. (Japanese)

Principle of Multichannel Electrode System and It's Application to the Crevice Corrosion in the Salt Manufacturing Plant

A. Naganuma and K. Azumi

Bulletin of the Society of Sea Water Science, Japan, **65** [2], 70-74 (2011)

Corrosion protection of steels used in salt manufacturing plants has been difficult task because of its severe corrosion condition in a high temperature corrodible solution containing saturated NaCl and $MgCl_2$. Crevice corrosion behavior of stainless steels of SUS316L, NAS64, NAS185N and NAS256N in saturated NaCl solution at a high temperature up to 100 °C was therefore investigated by using a multichannel electrode system. The artificial crevice was constructed using a pile of five sample sheets with a through hole and the coupling current between these five sheets were measured during the proceeding of the crevice corrosion. Spatial distribution of coupling current was measured as a function of depth in the artificial crevice and revealed the progress of the crevice corrosion as a function of kinds of steels, temperature, DO value and their cycling. In this explicative article, concept of the artificial crevice corrosion system, the principle of multichannel measurement system and interpretation of the experimental results were introduced. (Japanese)

Mechano-electrochemistry of a passive surface using an in-situ micro-indentation test

K. Fushimi, T. Shimada, H. Habazaki, H. Konno, M. Seo

Electrochim. Acta, **56**, 1773-1780 (2011)

Depassivation–repassivation of iron surfaces in boric–borate solutions were investigated by using the micro-indentation test. A pair of current peaks due to repair of the passive film following rupture of the film were observed during a series of indenter drives, i.e., loading and unloading of the indenter. The shape of the current peak depended on environmental conditions (conductivity and pH of the solution) and substrate conditions (mechanical processing history, alloyed element) as well as indentation conditions (repetition, maximum depth, and maximum load). Plastic deformation of the surface was accompanied by surface depassivation, while no depassivation occurred during the elastic deformation, indicating that the passive film on iron has a ductile property. The solution conditions did not affect the scale of depassivation but affected the rate of repassivation. Dislocations in the substrate made surface depassivation difficult but enhanced reactivity during the repassivation. The test also revealed that type-312L stainless steel has high corrosion resistance in a concentrated NaCl solution.

Investigation of Depassivation-repassivation Behavior of Metal Surfaces Using Micro-indentation test

T. Shimada (Yamamoto), K. Fushimi

Zairyo-to-Kankyo, **60**, 28-38 (2011)

A micro-indentation test was developed to investigate mechano-electochemical properties of metal surfaces. In solution environment, the contact of an indenter with an iron passive surface causes depassivation of the surface when the surface deforms plastically. The scale of the depassivation is dependent on hardness and deformation area of the substrate iron. Repassivation following depassivation is affected by not only electrode potential of the specimen and solution conditions (pH and electric conductivity of the solution) but also dislocation in the substrate iron. Furthermore, the micro-indentation test is useful as a rupture technique of the passive film in order to examine the corrosion resistance of stainless steels. It enables to control the deformation area of metal surfaces at an intentional site in a micrometer-order and to serve an in-situ measurement of electrochemical responses. This technique is suitable for consideration of the mechanism and kinetics of depassivation-repassivation behavior of the surface depending on fine metal structures.

Simple Heat Treatment for Fabrication of Carbonaceous Layer-coated Microelectrodes and Conductive Stainless steels

K. Fushimi, A. Ono, K. Matsushita, H. Kumagai, H. Konno

Appl. Surf. Sci., **257**, 8289-8294 (2011)

A simple heat treatment was used to fabricate carbonaceous layer-coated electrodes: micro-ring electrodes and conductive stainless steel. Substrates of sharpened quartz capillaries or type-316 stainless steel plates were put in an alumina boat with powder of petroleum pitch A240F separately and heated at 1073–1273 K in a flow of nitrogen or argon. By this treatment, both of the substrates were coated with a uniform carbonaceous layer of several hundred nano-meters in thickness. The electric conductivity of the layer was improved by increases in temperature and period of the heating. The quartz glass-capillary covered with the conductive layer was modified to a needle-type microelectrode by coating with an insulating polymer and baring the tip. At least a dozen carbon micro-ring electrodes with an outer radius of about 1 μm were successfully prepared by the simple heat treatment. On the other hand, the carbonaceous layer formed on type-316 stainless steel showed relatively poor conductivity due to the formation of oxides in the layer. However, the conductivity was improved by electroplating of nickel on the substrate before the heating. The carbonaceous layer-coated stainless steel showed good corrosion resistance in sulphuric acid.

Shielding Effect of Double Microelectrode Tips in a Scanning Electrochemical Microscope

K. Fushimi, K. Matsushita, Y. Hasegawa

Electrochim. Acta, **56**, 9602-9608 (2011)

Electrochemical interaction of coaxial double microelectrodes, in which a ring microelectrode was surrounded by another ring microelectrode, was investigated. Mass-transfer reactions that occurred on both inner and outer microelectrodes interfered with each other and showed a “shielding” effect depending on potentials and geometries of microelectrodes. Application of the inner microelectrode of the double microelectrodes for a probing tip of a scanning electrochemical microscope (SECM) revealed that the shielding effect by the outer microelectrode affected the electrochemistry on the inner microelectrode in the vicinity of the substrate surface.

The effect was intensified above the insulator but attenuated above the conductor as the microelectrodes approached in feedback mode of the SECM. Approach to a critical inter-electrode distance also intensified the shielding effect in the substrate generation/tip collection mode. An SECM line-scan using a platinum/epoxy resin-model substrate was carried out to investigate the shielding effect on current sensitivity and lateral resolution of an SECM image.

SECM Observation of Polycrystalline Iron Corroding in Sulphuric Acid Solution

K. Fushimi, K. Matsushita, H. Tachikawa, Y. Hasegawa

Proceedings of 18th International Corrosion Congress, 377.pdf (2011)

In order to investigate the non-uniform corrosion behaviour of polycrystalline pure iron in sulphuric acid, SECM of multi grains and a dynamic polarization test of single grains were carried out. SECM successfully visualized the difference in dissolution activity between 0 0 1 and 3 2 5 grains. The corrosion potential and corrosion current of the single grain were found to be dependent on the orientation. The grain showing a noble corrosion potential allowed a high corrosion current to flow. The sequence of corrosion activity of the lower Miller indices grains was in the order of 1 0 1 < 1 1 1 < 0 0 1, although both cathodic and anodic Tafel slopes were independent of the crystallographic orientation. The results indicated that hydrogen evolution reaction (HER) coupling with iron dissolution reaction governed the corrosion reaction on iron grains. A grain on which HER is more active than that on others, such as a 0 0 1 grain, plays an important role as cathodic parts for the heterogeneous corrosion of polycrystalline iron at corrosion potential. The dependence of relaxed surface on orientation is discussed from the viewpoint of HER activity using the results of *ab initio* calculation.

Heterogeneous Dissolution of Polycrystalline Pure Iron in Sulphuric Acid Solution

K. Fushimi, K. Matsushita, K. Miyamoto, Y. Hasegawa

Proceedings of EUROCORR 2011 (the European Corrosion Congress), www.eurocorr.org, 4747.pdf (2011)

Heterogeneous dissolution behaviour of a polycrystalline pure iron in sulphuric acid (pH 1 or 2.3) was investigated by a simple polarization technique and scanning electrochemical microscopy (SECM). Both corrosion potential and corrosion current on a single grain were found to be dependent on crystallographic orientation of the iron grain. A high corrosion current flowed on a grain showing a relatively noble corrosion potential, although both cathodic and anodic Tafel slopes were independent of the orientation. It was shown that cathodic hydrogen evolution reaction (HER) governed the corrosion reaction on the iron grain. On the other hand, an SECM image visualizing the generation of Fe^{2+} ions from the polycrystalline iron revealed that the iron dissolved heterogeneously corresponding to the grain orientation. The dissolution reactivity of each grain was different from the corrosion reactivity obtained by the simple polarization of the single grain. It was suggested from the comparison that the heterogeneous dissolution was due to the difference in HER reactivity of grains. Covalent bonding of Fe and H and coverage of H on Fe seemed to play important roles in the local HER leading to the heterogeneous dissolution of polycrystalline pure iron.

Repassivation Behavior of Titanium in Artificial Saliva Investigated with a Photon Rupture Method

M. Sakairi, M. Kinjyo and T. Kikuchi

Electrochimca Acta, **56**, 1786-1791 (2011)

Repassivation kinetics of titanium were investigated in artificial saliva by the photon rupture method, PRM, combined with anodizing. PRM uses focused pulsed Nd–YAG laser beam irradiation to remove oxide film and metal. The effects of the applied potential and F− ions on the repassivation kinetics of titanium were examined electrochemically. All conditions in this study use specimens that were repassivated within about 100 ms after the laser beam irradiation. The current transients after the laser beam irradia- tion showed a rapid increase, followed by a decrease with a slope of the log i vs. log t plots of about −1.5. The measured slope is steeper than what would be expected with the high field oxide film formation theory. This result suggests that the oxidation of titanium takes place through a combination of electro-chemical and chemical reactions. More NaF results in a higher peak current density and amount of charge after laser beam irradiation. The influence of F− ions on the repassivation kinetics may be explained by localized pH changes caused by dissolution of titanium immediately after the laser beam irradiation.

SCC Mechanism near fusion line of low C - 13%Cr welded joints

S. Hasizume, T. Nakayama, M. Sakairi and K. Fushimi

Zairyo-to-Kankyo, **60**, 196-201 (2011)

Low Carbon-13%Cr martensitic stainless steels have been widely used for line pipe application because of their high strength and excellent corrosion resistance in corrosive conditions. Recently, both laboratory and field experiences related to cracking near fusion line of these steels weld joints in hot acid environments have been published. In this paper, SCC mechanism near fusion line of low C – 13%Cr welded joints is discussed. Especially, initiation process is focused. Mainly electrochemical measurement using solution flow type micro-droplet cell and surface analysis of weld joints are conducted. Metallurgical examination and SSRT are also conducted to support understanding SCC mechanism. In the evaluation of electrochemical behavior of low C – 13%Cr welded joints with and without PWHT (Post Welded Heat Treatment) by the use of a solution flow type micro-droplet cell, PWHT leads to more noble and stable potential in HAZ compared to as-welded condition. In the HAZ portion of the as-welded joint, Cr depleted layer was detected under welding scale with the use of GDS (Glow Discharge Spectrometer). PWHT was confirmed to eliminate Cr depleted layer under welding scale. This can be an initiation of SCC near girth welded joint in hot acid environment. Finally, mechanism of SCC initiation near fusion line of as welded joint was proposed. Localized corrosion would start at Cr depleted layer under welding oxide scale. This dissolution was also accelerated by a galvanic effect due to a large cathode area of base metal.

Corrosion resistant TiO_2 film formed on magnesium by liquid phase deposition treatment

R. Fujita, M. Sakairi, T. Kikuchi and S. Nagata

Electrochimca Acta, **56**, 7180-7188 (2011)

Liquid phase deposition treatment (LPD) was applied to form a corrosion protective titanium dioxide (TiO_2) film on commercially available pure magnesium. Changing the solution pH, from acidic to highly alkaline, and with the addition of sucrose, it becomes possible to form a highly adhesive and thin TiO_2 film on commercially available pure magnesium without any heat treatment. The role of the sucrose may be

attributed to the formation of tetrafluoroboric acid $(BF_4)^-$ in the solution reducing the homogeneous nucleation of TiO_2 in the LPD solution. The film formed in the weak alkaline environment shows better corrosion resistance than at other LPD conditions, while the average rest potential is the same as that of as-polished specimens. This low rest potential may be due to micro-cracks in the formed film and high activity of the magnesium substrate.

Alkali Leaching of Ni-Al alloy Microchannel Lining Layer

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

J. JSEM Special Issue, **11**, SS276-SS279 (2011)

We investigate alkali leaching of Ni-Al alloy microchannel lining layers to produce a metallic microreactor for high- temperature catalytic reactions. The microchannels and the lining layers were produced by a powder-metallurgical microchanneling process with Ni powder and Al wires. We explored the conditions for the process to produce an Al_3Ni or Al_3Ni_2 lining layer. The Al concentration of the lining layers was successfully decreased by alkali leaching.

Local Cu electro-plating on non-conductive substrate and fabrication of metal structure with solution flow type micro-droplet cell

M. Sakairi, Y. Goto, T. Kikuchi and K. Fushimi
J. Surf. Fin. Soc. JPN, **63**, 551-515 (2011)

Solution flow type micro-droplet cell was applied to form local copper line on non-conductive substrate such as epoxy resin. A copper rod was mounted in epoxy resin as electric feeding point during copper deposition. The copper line was successfully formed on the epoxy resin not only flat surface but also curved surface. The formed copper line can remove from the epoxy resin, suggesting that this technique can be applied to form metal micro-structure. The influence of stage moving speed and applied current on thickness, shape and conductivity of formed copper line were also investigated. (Japanese)

Study on Hydrogen Storage System for Residential Energy System and Independent Power Supply with Hydrogen Absorbing Alloys and Air Heat Exchange Type Container Part 3 -Energy Conservation Effect and Installation Analysis of Passive Hydrogen Storage Systems for Fuel Cell CHP Systems

H. Shirato, Y. Hamada, T. Suda, M. Sakairi, Y. Oka, H. Hayashi, H. Ikeda and K. Nagano

Kukichyowa-Eisei kogaku, **171**(6), 1-7 (2011)

This paper is the third report of a series of research on passive type hydrogen storage system with hydrogen absorbing alloys. In this paper, we calculated energy conservation effect and executed installation analysis of the passive hydrogen storage systems that store and supply hydrogen from a reformer for fuel cell CHP (Combined Heat and Power) systems. Installation of the storage systems to the fuel cell CHP systems for residential energy systems enables to reduce start-up energy and primary energy for response to electric load change. It was showed that from several kg to maximum 15 kg of metal hydrides are necessary for the passive hydrogen storage systems and these systems are superior to batteries in terms of energy density, durability and initial cost. In conclusion, it was cleared that these systems are worth the installation for the fuel cell CHP systems.

Electrochemical detection of hydrogen generated by atmospheric corrosion of scratches in zinc coated steels -Effect of the scratched area-

S. Takagi and M. Sakairi

Zairyo-to-Kankyo, **60**, 435-437 (2011)

A micro-electrochemical cell for detecting permeated hydrogen by atmospheric corrosion was developed. Using this cell, the influence of the area of scratches on the hydrogen generated by the corrosion was investigated. Formation of galvanic couples between steel substrate and coating plays an important role on the generation on the hydrogen during atmospheric corrosion, and the amount of permeated hydrogen increases with larger areas of scratches.

Anodizing of the Inner Wall of the Microchannel Formed in Sintered Aluminum Body

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

J. JSEM Special Issue, **11**, SS267-SS271 (2011)

A fabrication method of a nanoporous anodic alumina film on the inner wall of a microchannel was investigated. An open microchannel was produced by a powder-metallurgical microchanneling process using Al as a body metal and Zn as a sacrificial-core metal. However, the cross-sectional area of the microchannel was larger than that of the sacrificial core; it increased as the compacting pressure increased. The nanoporous alumina film was produced by anodic oxidation of the inner wall of the microchannel.

Dealloying of Cu-Zn alloy Microchannel Lining Layers for Producing Microporous Catalyst

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

J. JSEM Special Issu, **11**, SS280-283 (2011)

A Cu-Zn alloy microchannel lining layer was fabricated by a powder-metallurgical process using Cu powder and Zn wire. The effects of the dealloying treatment on the composition and structure of the lining layer were investigated. The lining layer became more porous and dezinced as the dealloying time increased. In the case of long-time dealloying, Zn-based corrosion products precipitated. These results indicated the possibility of the control of the structure and composition of the inner wall of the microchannel.

Area Selective Formation of Porous Type Aluminum Anodic Oxide Film by a Solution flow-type Micro Droplet Cell

T. Murata, Y. Gogo, M. Sakairi, K. Fushimi and T. Kikuchi

ECS Transactions, **33**(16), 57-63 (2011)

A novel solution flow-type micro droplet cell with co-axial dual capillary tubes (Sf-MDC) was applied to form porous type aluminum anodic oxide film locally. This

technique makes it possible to form porous type anodic oxide film on aluminum locally. When the droplet cell remains stationary, the oxide film was growing both vertically and laterally. The growth rate in the lateral direction can be controlled by moving the droplet cell. By moving the droplet cell, a porous type anodic oxide film line was successfully formed. The thickness of the oxide film increases with decreasing scanning speed of the cell. The oxide film growth rate was greatly affected by specimen temperature.

Effect of magnesium ions on the corrosion behaviour of A3003 in simulated tap water

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

Proc. of EUROCORRO 2011, **4701**(5 pages) (2011)

The synergy effect of Mg^{2+} and Na^{+} on corrosion behavior of aluminum alloy (A3003) in model tap water was investigated by electrochemical noise and potential sweep polarization techniques. The galvanic current and specimen potential were measured for 86.4 ks. Fluctuations in the potential decreases and the galvanic current increas-es were measured, and the current fluctuations and potential fluctuations showed good correlation. After the experiments, corrosion products and micro pits were ob-served on the sample surfaces. A fluctuation may be attributed to an event of pitting corrosion, showing the birth, propagation and discontinuation of the pitting process. The amplitude of fluctuations of both current and potential was multiplied by coexis-tence of Mg^{2+} and Na^{+}. The total amount of charge passed during the galvanic corro-sion tests also increased with coexistence of Mg^{2+} and Na^{+}. This result suggests that coexistence of Mg^{2+} and Na^{+} acts as corrosion accelerators. This synergy effect of cations in model tap water may affect by the specimen potential.

Influence of cations on corrosion behaviour of aluminium alloys in drinkable water and model tap water

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The corrosion behaviour of aluminium alloys in small amounts of chloride ions containing solutions was examined by focusing on the effect of added cations and solution pH (buffer reaction of added 0.5 kmol/m^3 H_3BO_3/0.05 kmol/m^3 $Na_2B_4O_7$).

The effect of Cu deposition on corrosion behaviour of aluminium alloys was also investigated. The 3003 aluminium alloy shows lower corrosion resistance than 5005 aluminium alloy in the tap water and model tap waters. Corrosion of aluminium alloys is accelerated by addition of Ca^{2+} ions to the model tap waters especially at low pH. This behaviour may be explained by H^+ concentration increases caused by $CaCO_3$ formation. Without Cl^- ions, Cu^{2+} ions do not increase the corrosion rate of the aluminium alloys.

Composition Change in Al_3Ni_2 Microchannel Lining Layers by Alkali Leaching

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The relationship between the alkali leaching time and the composition change in the Al_3Ni_2 microchannel lining layer produced by the sacrificial-core method was investigated. The composition was measured both on the specimen surface directly exposed to the leachant and on the new surface cut after alkali leaching. The decreases in Al concentration become sluggish after formation of Ni_3Al. The alkali-leached lining layer remarkably oxidizes due to increase in specific surface area by alkali leaching.

Application of Pulsed Laser Fabrication in Localized Corrosion Research, Lasers - Applications in Science and Industry

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Aluminum and its alloys have been known as light metals because they are used to reduce the weight of automobiles and components. Aluminum is the second most used and produced metal in the world nowadays. It is well known that one of the typical corrosion morphologies of aluminum alloys in chloride containing environments such as seawater is pitting corrosion. Many papers have been investigating pitting corrosion. Electrochemical techniques, such as model macro-pits and electrochemical noise analysis have been applied to investigate pitting corrosion of aluminum alloys.

Details of the propagation of pitting corrosion are not fully understood, however, the aspect ratio of pits (pit depth/pit diameter) plays a very important role in the growth of corrosion pits. To understand this effect, an in-situ artificial pit fabrication technique with area selective dissolution measurements would be helpful. One such technique is pulsed laser fabrication, which uses focused pulsed Nd-YAG laser beam irradiation to remove material from the substrate, combined with anodizing. Some of the authors have reported on the electrochemical behavior of artificial pits fabricated on aluminum alloy.

In this chapter, the results of the effect of aspect ratio on dissolution behavior of the artificial pits formed on aluminum alloys are explained, and the chapter also explains the rate of pit fabrication and how to activate only the bottom surface of the formed pits.