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CURRENT ACTIVITIES and PRESENTATIONS

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Dr. Hyono has been joined as an assistant professor in our laboratory since the 1st of November 2010.

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

Research programs in progress are as follows:

(1) New corrosion resistive films consisting of conductive polymers

A conductive polymer coating was applied to corrosion prevention of magnesium alloy and carbon steel. The magnesium alloy was firstly covered by zinc electrodeposit and then by conducting polypyrrole (PPy) layer. Slight improvement of anti-corrosivity was performed. The steel coated by the PPy layer was exposed in humidified air in the presence of sodium chloride deposition to survey the protection property of the PPy layer.

(2) Pd electrode for application of PEFC cathode

Oxygen reduction reaction (ORR) was studied on Pd electrodes. The single crystals of Pd with (111), (110), and (100) surfaces and poly-crystalline Pd was used. Pt monolayer was formed on Pd electrodes by using Cu upd layer followed by replacement of Pt. The ORR current on Pd electrodes were smaller than Pt electrode and, however, the Pt monolayer on Pd much improved the ORR current. When two monolayers of Pt were formed on Pd, the ORR current is comparable to that of Pt electrode.

(3) Electrodeposition of Al-Zn alloys in chloride molten salt

Al-Zn-X(X=Mo, Mn) alloys were electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $ZnCl_2$ and $MoCl_3$ or $MnCl_2$ for corrosion protection of steel. The electrodeposition was performed by constant potential electrolysis or potential pulse electrolysis. The Zn content in the alloy gradually increases from 2 to 95 at% at potential from -50 to 100 mV (vs. Al/Al(III)). The Mo content increases from 0 to 3 at% at the same potential region. The surface morphology of the deposit was flat however some cracks exist in the deposit surface.

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

Glass plates were immersed in a molten salt of KNO_3-$TlNO_3$ at 698-723 K. During the immersion, ion-exchange was induced at the surface of the glass. By the reduction of the glass, Tl ion changed to metallic Tl and then the glass exhibited strong light absorption in visible light from 400 to 700 nm wavelength.

(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 investigated electrolytic melts for the process and were selected propylene carbonate or NaTFSI 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) Composition of passive oxide on type 304 stainless steel (SS) by XPS

The passive oxide on 304 SS in 0.1 M sulfuric acid solution was investigated by XPS. Cr content was seen to be enriched in the oxide to about 60% after 30 min by constant potential oxidation. The transient to the Cr enrichment was pursued and when one oxidized for time period longer than 30 min, the enrichment of Cr was retained to 60%.

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

Type 316L SS was immersed in pure water under 295 C-7.8 MPa for 1-7 days. Oxygen gas concentration in the water was controlled from 0.75 to 3.0 ppm. The oxide film formed was examined by multiple-angle-of–incidence ellipsometry for the thickness, GD-OES for the depth profile, and Raman spectroscopy for the composition estimation. The film consisted of two layers, the inner layer of which was composed of Cr-Fe spinel and the outer of $\alpha-Fe_2O_3$. The thickness of the outer layer much depended on the oxygen concentration, while the inner layer did not. The inner layer may be formed by a direct reaction between the SS substrate and water/ oxygen. The outer layer may be formed by oxidative deposition from ferrous ions dissolved.

(8) Micro-ellipsometry for application to ununiformity of the passive oxide

A micro-ellipsometry was newly designed for the study of the ununiformity of the thin passive oxide on titanium and type 304 SS under in-situ condition. An optical microscope with a CCD camera was equipped to the null-method ellipsometry. During the oxide growth, the bright sites appeared and brightness of the sites depended on the film thickness at individual sites. For the film growth of titanium by anodic oxidation, the thickness of the films was seen to greatly depend on the orientation of grains. For the pitting initiation on the SS, the change of the film in thickness was observed before the pit generation.

Other Activities

Assoc Prof. Ueda attended the Euchem2010, Bamberg, Germany, March 15-19, International conference on functional nanocoatings, Dresden, Germany, March

28-30 and the ECS annual meeting, Las Vegas, USA, Oct.10-15, 2010, and presented papers entitled by " Fabrication of Functional Glass by Ion-exchange Treatment in Nitrate Molten Salts", "Fabrication of Functional Glass by Ion-exchange Treatment in Nitrate Molten Salts" and “Surface Finishing of Mg Alloys by Al Electroplating in $AlCl_3$-EMIC Ionic Liquid”.

Assistant Prof. Hyono attended JSPS-DST Asian Academic Seminar 2010, Kolkata, India, Nov.29- Dec.4.

Presentations

Formation of Nano-Particle in a Glass by Ion-Exchange Treatment, M. Ueda, BMMP2010, Nagoya University, Nagoya, January 27, 2010

Electroplating using polypyrrole electrode-effect of plating condition for deposition behavior of metal particle, T. Kikuchi, M. Ueda, M. Sakairi, T. Yonezawa, The 121st Meeting of The Surface Finishing Society of Japan, Seikei University, Musashino, March 15-16, 2010

Fabrication of Functional Glass by Ion-exchange Treatment in Nitrate Molten Salts, M. Ueda, Euchem2010, Bamberg, Germany, March 18, 2010

Electroplating of aluminum alloys for improving oxidation resistance of TiAl intermetallics, M. Ueda, International conference on functional nanocoatings, Dresden, Germany, March 29, 2010

Electrorefining of Na, M. Ueda, 21st meeting in electrolysis process committee, Doshisya University, Kyoto, June 26, 2010

Diffusion of Tl ion into a glass in ion-exchange treatment, M. Ueda, H. Matsunaga, T. Ohtsuka, T. Yamashita, Summer meeting 2010 of Hokkaido branch of The Chemical Society of Japan, Hakodate National College of Technology, Hakodate, July 24, 2010

Oxygen reduction on Pt-Pd electrode as a PEFC cathode, Y. Sugawara, M. Ueda, T. Ohtsuka, Summer meeting 2010 of Hokkaido branch of The Chemical Society of Japan, Hakodate National College of Technology, Hakodate, July 24, 2010

Formation of polypyrrole layer on magnesium alloys covered by zinc, N. Sheng and T. Ohtsuka, Summer meeting 2010 of Hokkaido branch of The Chemical Society of Japan, Hakodate National College of Technology, Hakodate, July 24, 2010

Deposition behavior of Pd fine particles on polypyrrole electrode, T. Kikuchi, M. Ueda, M. Sakairi, T. Yonezawa, A meeting 2010 of Hokkaido branch of The Chemical Society of Japan, Hakodate National College of Technology, Hakodate, July 24, 2010

Observation of corrosion surface on metals using micro-ellipsometry, K. Yamanaka, M. Ueda, T. Ohtsuka, Fall Meeting of ECSJ 2010, Kanagawa Institute of Technology, Atsugi, September 2-3, 2010

Al electroplating on Mg alloys using low-temperature ionic liquid, M. Ueda, Y. Tabei, T. Ohtsuka, The 122nd Meeting of The Surface Finishing Society of Japan, Tohoku University, Sendai, September 6-7, 2010

Anodic reaction on carbon electrode in LiOH-LiCl mixture molten salt, K. Wakai, M. Ueda, T. Ohtsuka, The 42nd Symposium on Molten Salt Chemistry, Loisir Hotel Hakodate, Hakodate, September 9-10, 2010

Insertion of Tl ion into glass from a molten salt and formation of Tl nano particles, H. Matsunaga, M. Ueda, T. Ohtsuka, T. Yamashita, The 42nd Symposium on Molten Salt Chemistry, Loisir Hotel Hakodate, Hakodate, September 9-10, 2010

Deposition and dissolution reactions of sodium in TBA-TFSI ionic liquid containing Na^+, Y. Numata, M. Ueda, T. Ohtsuka, The 42nd Symposium on Molten

Salt Chemistry, Loisir Hotel Hakodate, Hakodate, September 9-10, 2010

Electrochemical reaction of Na in NaTFSI-TBATFSI ionic liquid, Y. Numata, M. Ueda, T. Ohtsuka, The 147th Fall meeting of the Japan institute of metals, Hokkaido University, Sapporo, September 25-27, 2010

Decrease of Ca content in Na electrorefining using ionic liquid, K. Honda, M. Ueda, T. Ohtsuka, The 147th Fall meeting of the Japan institute of metals, Hokkaido University, Sapporo, September 25-27, 2010

Effect of sulfate and chloride ions on the composition of rust on weathering steel, T. Ohtsuka and S. Tanaka, 160th Fall meeting of ISIJ, Hokkaido University, Sapporo, September 25-27, 2010.

Development of recycle technique for used sodium-sulfur secondary battery, M. Ueda, Innovation Japan 2010, Tokyo International forum, Tokyo, September 29 - October 1, 2010

Surface Finishing of Mg Alloys by Al Electroplating in $AlCl_3$-EMIC Ionic Liquid, M. Ueda, 218th ECS Meeting, Riviera Hotel, Las Vegas, U.S., October 10-15, 2010

Electrochemical measurement of Pd electrode covered with Pt mono-layer for cathodic oxygen reduction, Y. Sugawara, M. Ueda, T. Ohtsuka, 57th Symposium on Materials and Environments, Naha, Okinawa, October 20-22, 2010.

Non-uniformity evaluation of passive film by ellipsometry microscope, K. Yamanaka, M. Ueda, T. Ohtsuka, 57th Symposium on Materials and Environments, Naha, Okinawa, October 20-22, 2010.

Poly-pyrrole electrodeposition on magnesium alloy of AZ91D alloy in aqueous media, N. Sheng and T. Ohtsuka, 57th Symposium on Materials and Environments, Naha, Okinawa, October 20-22, 2010.

Development of recycle technique for used sodium-sulfur secondary battery, M. Ueda, The 24th Business Expo, Access Sapporo, Sapporo, November 11-12, 2010

Development of functional glass by ion exchange treatment in molten salt, M. Ueda, The 24th Business Expo, Access Sapporo, Sapporo, November 11-12, 2010

Reduction process of cupric oxide and cuprous oxide to metallic copper fine particles, A. Hyono, N. Nishida, and T. Yonezawa, 35th Anniversary of Division of Colloid and Interface Chemistry, The Chemical Society of Japan, September 19-22, 2010

Facilities and Capabilities

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light and null-method ellipsometer for multiple-angle-of-incidence measurement
Potential Modulation Reflectance: Wavelength region from 350 to 800 nm
Raman Scattering Spectrometer: Bonko Keiki, single type of spectrometer equipped by high sensitive CCD
FT-IR Spectrometer: JASCO FT/IR 4200 equipped with MCT detector, IR-RAS apparatus, and IR microscopy system.
QCM system for in-situ gravimetry of surface layer on metals
Electrochemical AC Impedance: NF Circuit Design 5020 FRA and 5095 FRA equipped with a specially designed potentiostat
ICP atomic emission spectrometer: Thermo i-CAP 6000
Carl Fischer moisture measuring system: Metrohm 852 titrando
Evaporator: Eyela SB1100
Electrochemistry apparatuses
Optical Microscopy
Electrochemical Corrosion Rate Monitor System
Molten salt ion-exchange apparatus for glass
Luminescence apparatus for thin surface layer equipped with He-Cd UV laser

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Professor Soo-Gil Park, Dean of Research Center of Energy Storage, Chungbuk National University, stayed as a visiting Professor from July 2009 and left in February 2010. Dr Alexander Mozalev joined our group in October as a JSPS fellow.

The research activities of the laboratory are directed towards the development of advanced oxide films and nanomaterials utilizing anodic oxidation process and spin casting. 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 follows:

(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 a first example of the proton-conducting anodic ZrO_2-WO_3 films.

(2) Tailoring of self-organized porous anodic oxides on various valve 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. Unique microcone-shaped nanoporous anodic niobium oxide films are also fabricated by simple anodizing in phosphate-glycerol electrolyte. Superhydrophobicity has been successfully realized using the anodic oxide microcones. Crystallization of the anodic oxide during anodizing is a key to form the microcone oxide films. We successfully controlled the morphology of the microcones by changing the anodizing conditions.

(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 organizer of two International Symposia: 10th International Symposium on Electrochemical/Chemical Reactivity of Metastable Materials (E-MRS 2010 Fall Meeting), Warsaw, Poland and Corrosion Science: Models and Mechanisms (ISE 2010 Annual Meeting), Nice, France. He attended 2010 International Conference on Advanced Capacitors, held in Kyoto in June and presented an invited lecture entitled “Synthesis of Valve

Metal Nanocolumns by Oblique Angle Physical Vapor Deposition for Electrolytic Capacitor Application". He also presented an invited lecture "Fabrication of superhydrophobic surfaces with dual scale pores" at 2nd Korea-Japan Joint Symposium of ARS and Capacitor, at Gyeongju, Korea in June.

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 0 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.

Presentation at International Symposia

H. Habazaki, "Synthesis of Valve Metal Nanocolumns by Oblique Angle Physical Vapor Deposition for Electrolytic Capacitor Application", 2010 International Conference on Advanced Capacitors, 31 May-2 June, Kyoto (2010)

T. Fujii, Y. Aoki, H. Habazaki, "Oblique Angle Physical Vapor Deposition of Al and Al-Nb Alloys for Electrolytic Capacitor Electrodes", 2010 International Conference on Advanced Capacitors, 31 May-2 June, Kyoto (2010)

M. Teraoka, Y. Aoki, S.G. Park, H. Habazaki, "Synthesis of lithium titanate films from porous anodic titania", 2nd Korea-Japan Joint Symposium of ARS and

Capacitor, 28th June, Gyeongju, Korea (2010)
S. Tsunekawa, Y. Aoki, H. Habazaki, "Plasma electrolytic oxidation coating on β-Ti alloy with high wear resistance and good adhesion", 2nd Korea-Japan Joint Symposium of ARS and Capacitor, 28th June, Gyeongju, Korea (2010)

H. Habazaki, T. Fujii, S. Yang, Y. Aoki, "Fabrication of superhydrophobic surfaces with dual scale pores", 2nd Korea-Japan Joint Symposium of ARS and Capacitor, 28th June, Gyeongju, Korea (2010)

H. Habazaki, "Platelet-type carbon nanofibers: template-assisted synthesis and applications", Post-TOCAT6/APCAT5-24th CRC International Symposium –Novel Nanostructures and Catalysis-, 24-25th July, Toya, (2010)

H. Habazaki, M. T. Tanvir, Y. Aoki, "Oblique angle deposition of silicon-supersaturated titanium alloy nanopillar films for capacitor application", E-MRS 2010 Fall Meeting, 13-17 September, Warsaw University of Technology, Warsaw, Poland (2010).

S. Yang, T. Fujii, Y. Aoki and H. Habazaki, "Factors controlling morphology of self-organized nano-porous niobium oxide microcones by anodizing in hot phosphate-glycerol electrolyte", E-MRS 2010 Fall Meeting, 13-17 September, Warsaw University of Technology, Warsaw, Poland (2010).

T. Fujii, Y. Aoki, H. Habazaki, "Liquid repellency of surfaces with dual-scale pores developed by oblique angle deposition and anodizing", E-MRS 2010 Fall Meeting, 13-17 September, Warsaw University of Technology, Warsaw, Poland (2010).

Y. Aoki, K. Ogawa, Y. Fukubaga, H. Habazaki and S. Yamaguchi, "Proton conductivity transition of amorphous zirconium phosphate thin film and its application to thin film fuel cell", E-MRS 2010 Fall Meeting, 13-17 September, Warsaw University of Technology, Warsaw, Poland (2010).

H. Habazaki, T. Fujii, Y. Aoki, "Fabrication of Superhydrophobic Surfaces with Dual Scale Pores by Oblique Angle Deposition and Anodizing", 8th International Symposium on Electrochemical Micro & Nanosystem Technologies, 21-14

September, Pierre & Vacances Cannes Mandelieu Resort, Cannes, France (2010).

H. Habazaki, Y. Konno, Y. Aoki, “Growth Behaviour of Porous Anodic Films on Iron in Fluoride-Containing Ethylene Glycol Electrolyte”, 27 Septermber-1 October, 61th ISE Annual Meeting, Palais des Congrès Acropolis, Nice, France (2010).

F. Di Quarto, M. Santamaria, H. Habazaki, “Characterization of Anodic Oxides on Magnetron Sputtered Ta-Nb Alloys by Photocurrent Spectroscopy and Differential Admittance Measurements”, 27 Septermber-1 October, 61th ISE Annual Meeting, Palais des Congrès Acropolis, Nice, France (2010).

F. La Mantia, H. Habazaki, M. Santamaria, F. di Quarto, “A Critical Analysis on the Use of Mott-Schottky Plots to Characterise the Passive Film/Electrolyte Junction” 27 Septermber-1 October, 61th ISE Annual Meeting, Palais des Congrès Acropolis, Nice, France (2010).

H. Habazaki, S. P. Sah, Y. Tarsuno, K. Fushimi, Y. Aoki, “Analysis of Dielectric Breakdown Films on Aluminium Formed by Single Pulse Anodizing”, 27 Septermber-1 October, 61th ISE Annual Meeting, Palais des Congrès Acropolis, Nice, France (2010).

T. Yamamoto, K. Fushimi, H. Habazaki, H. Konno, “Current Transients from Anodized Aluminum Surface using Micro-indentation Test in Borate Solution”, 27 Septermber-1 October, 61th ISE Annual Meeting, Palais des Congrès Acropolis, Nice, France (2010).

T. Fujii, Y. Aoki, H. Habazaki, “Surface micro-/nano-morphology for superoleophobicity”, Nagoya Univ.-Tsinghua Univ.-Toyota Motar Corp.-Hokkaido Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st Century –, 709 October, Hokkaido Univ. (2010) (invited)

K. Ye, Y. Aoki and H. Hbazaki, “High proton conductivity in anodic ZrO_2-WO_3-SiO_2 nanofilms” Nagoya Univ.-Tsinghua Univ.-Toyota Motar Corp.-Hokkaido Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st

Century –, 709 October, Hokkaido Univ. (2010)

S. Yang, T. Fujii, Y. Aoki, H. Habazaki, "Micro-/nano-hierarchical morphology of self-organized anodic oxides, Nagoya Univ.-Tsinghua Univ.-Toyota Motar Corp.-Hokkaido Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st Century –, 709 October, Hokkaido Univ. (2010)

Y. Fan, Y. Aoki, H. Habazaki, "Thickness-dependent proton conductivity in anodic ZrO_2-WO_3 nanofilms", Nagoya Univ.-Tsinghua Univ.-Toyota Motar Corp.-Hokkaido Univ. Joint Symposium –Materials Science and Nanotechnology for the 21st Century –, 709 October, Hokkaido Univ. (2010)

S. Koyama, Y. Aoki, H. Habazaki, "Capacitance enhancement of anodic ZrO2 film by incorporation of foreign species", 4th GCOE International Symposium - towards a sustainable future-, 24-25 November, Hokkaido Univ., (2010)

S. Yang, Y. Aoki, H. Habazaki, "Morphological control of self-organized anodic niobium oxide microcones", 4th GCOE International Symposium - towards a sustainable future-, 24-25 November, Hokkaido Univ., (2010)

K. Ye, Y. Aoki, S. Nagata, H. Habazaki, "High proton conductivity in anodic ZrO_2-WO_3-SiO_2 nanofilms", 4th GCOE International Symposium - towards a sustainable future-, 24-25 November, Hokkaido Univ., (2010)

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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) structures of oxide scales formed on carbon steels and stainless steels in H_2O-containing atmospheres, 3) high-temperature oxidation behavior of silicides, 4) characterization of scale failure by detecting acoustic emission (AE), 5) sintering of nano WC-X, 6) development of hydrogen production method, and 7) development of new Pb-free solders.

Current topics on research are as follows:

(1) High-temperature corrosion behavior of high Si alloys

High-temperature corrosion tests of Cr-Si-Ni and CoNiCrAlY-Si alloys in molten Na_2SO_4 and NaCl salts are being carried out. These alloys have excellent corrosion resistance due to the formation of a protective SiO_2 scale. This result demonstrates that the SiO_2 scale is very effective for preventing sulfidation and chlorination of alloys.

(2) High-temperature oxidation of carbon steels and stainless steels in H_2O-containing atmospheres

In order to clarify the microstructures of oxide scales formed on steels and stainless steels, oxidation tests are being done in H_2O-containing atmospheres. These investigations are focused on the distribution of alloying elements such as Si, Mn, Al, Cr, and Mo in oxide scales and substrates.

(3) Oxidation behavior of metal disilicides

In order to clarify the effect of Ge addition on high temperature oxidation behavior of $NbSi_2$, oxidation tests of Ge added $NbSi_2$ are being done. The results demonstrated that the addition of Ge to $NbSi_2$ led to the formation of a protective SiO_2 scale, resulting in remarkable improvement of oxidation resistance of $NbSi_2$.

(4) Characterization of scale failure

Characterization of scale failure by detecting acoustic emission during cooling after annealing in air is in progress for Fe-Si alloys with some Si contents. The fracture mode changes from spallation of oxide scale at the scale/substrate in low Si steels to cracking inside oxide scale in high Si steels. The new parameter for characterizing the failure mode was proposed.

(5) Sintering of nano WC-X

Nano sized tungsten carbide (n-WC) compacts with and without grain growth inhibitors were synthesized by Spark Plasma Sintering with different heating rates. The microstructure and mechanical properties of the various samples were compared. Grain growth inhibition effects increased in the order Nb>Re>Ta>Ti and with increasing heating rate. On the other hand, addition of Si and B increases grain growth, but suppresses the formation of the brittle semi carbide (W_2C) phase.

(6) Development of new hydrogen production method

Development of a new method for the production of hydrogen is in progress. As the method, the NaOH/H_2O/metal system was proposed, and it was actually proved that the high efficient production of high purity hydrogen could be achieved. The mechanism is under consideration.

(7) Development of new Pb-free solders

In order to clarify the influences of composition and cooling rates on the microstructures of Sn-Ag-Cu solders, some Sn-Ag-Cu alloys were solidified at different cooling rates. 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 or In resulted in further refinement of primary and Sn-Ag_3Sn eutectic phases. The research on corrosion of iron-based alloys in molten lead-free solders such as Sn-Ag-Cu, Sn-Bi, Ag-Cu and Sn-Ag-Al is also in progress.

Other activities

In February, Prof. Kurokawa and Dr. A. K. Nanda Kumar attended The 17th Annual Meeting of IAPS International Workshop 2010 in Busan, Korea, and presented a paper entitled “The Sintering Kinetics of n-WC-Si and n-WC-B”. In September, Dr. Lobo at Group for Nanoscale Sci. & Nanotech., FCT/UNL, Portugal, visited our lab. for the research on hydrogen/metal interaction.

Presentations

High temperature corrosion behavior of STBA21 and Cr-Si-Ni compacts in molten Na_2SO_4 and NaCl salts; T. Sano, T. Sudiro, A. Yamauchi, S. Kyo, O. Ishibashi, M. Nakamori and K. Kurokawa: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Sapporo, Jan., 2010.

Damage behavior of scales oxidized on Si-containing low carbon steels – Influence of cooling rate –; H. Nakata, A. Yamauchi, S. Taniguchi, K. Kurokawa, Il-Ryoung Shon and Jin-Won Choi: ibid

Interfacial reaction of Sn-Ag-Cu micro joint using Ag electrode; A. Yamauchi, K. Kurokawa and J. Tanaka: ibid

Interfacial reaction behavior of Fe-based alloys with molten lead-free solder in various corrosion conditions; T. Kawamoto, A. Yamauchi, K. Kurokawa and J. Tanaka: 2010 Winter Joint Meeting Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem., Sapporo, Jan., 2010.

Variation of cooling rate on cast structure of Sn-Ag-Cu alloys; S. Kirai, A. Yamauchi, K. Kurokawa and J. Tanaka: ibid.

Effects of additional elements and cooling rates on microstructures of Sn-Ag-Cu solders; S. Kirai, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: Mate2010, Yokohama, Feb., 2010.

Analysis of reaction behavior of Fe-based alloys with additional elements in molten lead-free solders; T. Kawamoto, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: ibid.

The Sintering Kinetics of *n*-WC-Si and *n*-WC-B; A. K. Nanda Kumar, M. Watabe, A. Yamauchi and K. Kurokawa: The 17th Annual Meeting of Inst. of Applied Plasma Sci., Busan, Korea, Feb. 2010.

Influence of Ni concentration on high temperature corrosion behavior of Cr-Si-Ni compacts in molten Na_2SO_4 and NaCl salts; T. Sano, T. Sudiro, A. Yamauchi, S. Kyo, O. Ishibashi, M. Nakamori and K. Kurokawa: The 146th Annual Meeting of Jpn. Inst. Metals, Tsukuba, Mar., 2010.

Influence of cooling rate on the failure behavior of scale formed on Si-containing low carbon steels; H. Nakata, A. Yamauchi S. Taniguchi, K. Kurokawa, Il-Ryoung Shon and Jin-Won Choi: ibid.

Influence of Cooling Rate and Composition on the Microstructure of Sn-Ag-Cu Alloys; S. Kirai, A. Yamauchi, K. Kurokawa, and J. Tanaka: International

Conference on Electronics Packaging 2010, Sapporo, May, 2010.

Effect of Additional Elements on Corrosion Resistance of Carbon Steel in Molten Lead-Free Solder; T. Kawamoto, A. Yamauchi, K. Kurokawa, and J. Tanaka: ibid.

Effect of additional elements on subgrain structure in Sn-based alloys; A. Yamauchi, H. Takagi, and J. Tanaka: ibid.

Effect of Bi concentration on microstructural evolution and element distribution of Sn low Bi alloys; T. Yokota, A. Yamauchi, K. Kurokawa and J. Tanaka: The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Muroran, July, 2010.

Oxidation-resistant coating for Nb alloys; K. Kurokawa: The JWRI Meeting, Osaka, Aug., 2010

Effect of Si and SiC addition on the various properties of nano WC compact; K. Kimura, M. Watabe, A. Yamauchi and K. Kurokawa: ibid

Effect of Ni addition on structure of Sn-Ag-Cu/Cu Solder joint; A. Yamauchi and J. Tanaka: 20th Symposium of Micro Electronics, Kusatsu, Sep., 2010.

Relation between microstructure and hardness of Sn-low Bi alloys; T. Yokota, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: ibid.

High-temperature Corrosion of CoNiCrAlY-Si Alloys in a Na_2SO_4-NaCl Atmosphere; T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, A. Yamauchi and K. Kurokawa: The 147th Annual Meeting of Jpn. Inst. Metals, Sapporo, Sep., 2010.

Effect of Mo addition on the formation of Al_2O_3 scale formed on β-NiAl; T. Ito, K. Kurokawa and T. Narita: ibid.

The microstructure and sintering kinetics of n-WC-Si composites: A. K. Nanda Kumar, M. Watabe and K. Kurokawa: ibid.

Failure characteristic of scales formed on Si-containing low carbon steels during cooling –influence of cooling rate and water vapor; H. Nakata, A. Yamauchi S. Taniguchi, K. Kurokawa, Il-Ryoung Shon and Jin-Won Choi: International Symposium on High-temperature Oxidation and Corrosion 2010, Zushi, Nov. 2010.

High temperature oxidation of Nb disilicide; M. Ukegawa, S. Matsushita and K. Kurokawa: ibid.

High temperature corrosion behavior of Si-contaning alloys in the gas phase of O_2-(Na_2SO_4+ 25.7mass% NaCl); T. Sudiro, T. Sano, S. Kyo, O. Ishibashi, M. Nakamori, A. Yamauchi and K. Kurokawa: ibid.

Oxidation behavior of β-SiAlON in H_2O-containing atmosphere; A. Yamauchi X. Yi, T. Akiyama and K. Kurokawa: ibid.

Facilities and Capabilities

Spark Plasma Sintering Equipment
Ultra-High Vacuum Furnace with Mass Spectrometer
Oxidation Test Equipment with Thermobalance and Ultra-High Temperature Furnace
Optical Microscope with High-Temperature Furnace
SEM
Micro Vickers Hardness Tester
Acoustic Emission System

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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 follows;

(1) Biocompatibility and biomedical application of carbon nanotubes(CNT) and

other fine particles

Biocompatibility and cytotoxicity of carbon nanotubes(CNT), carbon nanofibers(CNF), fullerene and other nano materials were investigated. Various type of CNT including single and multiwall 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 Xray 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 fiberpolymer complex at 250 C or photopolymerization method. Biocompatible $CaOP_2O_5SiO_2Al_2O_3$ (CPSA) glass fibers of 820 μm in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bisGMA. 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 NiTi used in the initial stage of orthodontic treatments to CoCr 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 1100 μm 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 particlecontained tissue region and heal inflammation. For 13 μm the inserted region is never encircled with fibrous connective tissue layer and inflammation continues.

The in vitro cell functional tests on cell survial 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 neutrophis are inflated with more complicated polyacicular morphology. One of the marking cytokines released at phagocytization, TNFα, was not detected in any solution of Ni, V, Ti, the simulated body fluid(Hank's solution) mixed with 10 mm paricles of Ti and with submicron size Ni particles. TNFα was found only in the 13 μm 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 13 μm and 10 μm Ti particles suggests that the particles(13 μm) smaller than cell size(about 5 μm in neutrophils) induces cytotoxicity as a result of phagocytosis, while for particles larger than cell size (10μm) 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. Physicalmechanical 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 insitu 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 photopolymerized by scanning laser beam originally on the shallow depth of liquid epoxy monomer, was applied for the fabrication of dental prosthoses of photocuring 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 predesigned 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, γray from Co^{60} and electrons on one of the main matrix polymer UDMA(urethane dimethacrylate) for dental composite resin were investigated with various mechanical tests and spectroscopies. C^+ion radiation induced the large change in the structure sensitive properties of mechanical properties, Vickers hardness, flexural strength, abrasion resistance and little change in the nonstructure sensitive properties of spectroscopies, FTIR, 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 crosslinking 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 solgel method

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

(11) Tissues and dental materials observation by XSAM

The scanning Xray 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) Abrasionresistant implant made of refractory metal nitrides and carbides

Surfacenitrided titanium(Ti(N)) showed high corrosion resistance and nearly equivalent biocompatibility with Ti in soft and hard tissue in animal implantation test. Surface durability was evaluated by three static and dynamic mechanical tests; Vickers hardness test, Martens scratch test and for more practical viewpoint newly developed abrasion test using ultrasonic dental scaler which is used to remove calculus on teeth in dental clinics. Vickers hardness of Ti(N) was 1300, ten times larger than Ti. Martens scratch test showed that the bonding of nitrided layer with 2 μm 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 abrasionresistant implant materials for the application to the artificial joint of implant and abuttment part of dental implant.

(14) Development of visiblelight 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 visiblelight reactive photocatalysis. Visible light sesitization was obtained by surface modification with caions of Au, Ag, Cu, Pt, Pd. Depigmentation with visible light around 470 nm 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 resinrestored 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 resinrestored 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 600 nm 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 400 nm both teeth and resin showed the fluorescence emission with high and comparable intensity. For the light of 430,450 nm teeth emitted higher fluorescence and the relative difference is larger. The images formed with fluorescence light for more than 500 nm emitted by 430,450 nm 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(DLlactide co glycolide) and poly(LLactide), 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 shrinkageinduced 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.TaeSung BAE) on evaluation of mechanical properties of laserwelded Ti, dental porcelain, with Institute for Materials Science, Dresden Institute of Technology, GERMANY (Prof.W.POMPE) on the biocompatibility evaluation and application of collagenhydroxyapatite 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.

Presentations

XAFS analysis of strontium contained in human tooth, Uo M., The 27th PF symposium, Tsukuba, Mar. 2010.

Application of the rare earth containing yttria nanoparticles for dental materials, Uo M., Kanamori T., Takahashi M., Watari F., The 21st Functionally Graded Materials Symposium, Sapporo, July, 2010.

Analysis of metallic restorations of metal allergy patients, Uo M., Murata T., Furuhashi K., Notani K., Kitagawa Y., 3rd meeting of Nano Biomedical Society, Tsurumi, Sept. 2010.

Structural analysis of strontium in human tooth immersed in S-PRG eluate using XAFS analysis, Uo M., Abe S., Akasaka T., Watari F., Nakatsuka T., 56th Symposium of the Japanese Society of Dental Materials and Devices, Gifu, Oct. 2010.

Influence of Carbon Nanotubes on Biofilm Growth, Tsukasa AKASAKA, Shigeaki ABE, Motohiro UO, Fumio WATARI, the 55th General Session of the Japanese Society for Dental Materials and Devices, Tokyo, Apr.17-18, 2010

Cell Behavior in Different Cell Types on Thin Films of Carbon Nanotubes, Tsukasa AKASAKA, Shigeaki ABE, Motohiro UO, Fumio WATARI, the 56th General Session of the Japanese Society for Dental Materials and Devices, Gifu, Oct.9-10, 2010

Murine Macrophage Raw264.7 Cells Response for the Carbon Nanotubes Immobilized on Substrate, Tsukasa AKASAKA, Kouta ISHII, Makoto MATSUOKA, Takeshi HASHIMOTO, Toshio TAIRA, Fumio WATARI, the 23rd Annual and International Meeting of the Japanese Association for Animal Cell Technology, Sapporo, Sep.2-4, 2010

Cell Culture on Thin Films of Carbon Nanotubes, Tsukasa AKASAKA, Takeshi HASHIMOTO, Makoto MATSUOKA, Atsuro YOKOYAMA, Fumio WATARI, the 32rd Annual Meeting of the Japanese Society for Biomaterials, Hiroshima, Nov. 29-30, 2010

Cell adhesion to the materials treated with carbon nanotubes, Makoto MATSUOKA, Tsukasa Akasaka, Fumio Watari, Yasunori Totsuka, The 55th General Session of the Japanese Society for Dental Materials and Devices, Tokyo, Apr.17-18, 2010

3D scaffold coated with carbon nanotubes for tissue engineering; E.HIRATA, M.UO, Y.TAKITA, F.WATARI, A.YOKOYAMA, 88 th General Session of the IADR, Barcelona, Spain, July.16, 2010

Application of collagen sponge coated with multiwalled carbon nanotubes to 3D cell culturing and bone tissue engineering; E.HIRATA, M.UO, Y.TAKITA, F.WATARI, A.YOKOYAMA, 9 th Asian Academy of Osseointegration, Seoul, Korea, November 14, 2010

A DFT and MD study on the evaporation dynamics of water molecules on nanocarbon materials; Sigeaki Abe, Yoshinori Nagoya, Fumio Watari and Hiroto Tachikawa, EM-NANO 2010, Toyama, Jun. 2010

The interaction of carbon nanotubes with polypeptide: An *in vitro* and *in silico* study; Shigeaki Abe, Rika Komine, Yoshinori Nagoya, Fumio Watari, and Hiroto Tachikawa, Korea Japan Joint Forum 2010, Kitakyushu, Aug. 2010

3D structure of nanomaterial scaffolds for tissue engineering using electron and atomic force microscope; Shigeaki Abe, Hirohisa Kobayashi, Takayuki Kiba, Kosuke Ishikawa, Mami Mutoh, Tsukasa Akasaka, Motohiro Uo, Yasutaka Yawaka, Shin-Ichiro, Fumio Watari and Masaya Suzuki, NSS6, Kobe, Oct. 2010

Biodistribution of water-soluble Carbon Nanotubes in mice and its biocompatibility; Shigeaki Abe, Sachiko Itoh, Daisuke Hayashi, Atsushi Hyono, Tsukasa Akasaka, Motohiro Uo, Yasutaka Yawaka, Tetsu Yonezawa, Fumio Watari and Tomoya Takada, AsiaNANO 2010, Tokyo, Nov. 2010

Biodistribution of micro/nano-sized ceramics particles in mice; Shigeaki Abe, Nobuki Iwadera,Kouseke Ishikawa, Tsukasa Akasaka, Motohiro Uo, Yasutaka Yawaka, Yoshinori Kuboki, Tetsu Yonezawa, and Fumio Watari, 10th Asian BioCeramics Symposium, , Jogyakarta, Nov. 2010

Internal distribution of micro-/nano-sized inorganic particles and its cytocoxisity; Shigeaki Abe, Nobuki Iwadera, Kosuke Ishikawa, Atsushi Hyono, Sachiko Itoh, Tsukasa Akasaka, Motohiro Uo, Yasutaka Yawaka, Yoshinori Kuboki, Tetsu Yonezawa, and Fumio Watari, 3rd International Conference of Ceramics 2010, Osaka, Nov. 2010

Controlled Calcification Using Biomimetic Macromolecules; Shigeaki Abe. Yuhei Fujii, Arisa Kusuhara, Emi Yamatoya, Tomoki Ishida, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, Daisuke Hayashi, Tomoya Takada, ISACB2010, Cairns, Dec. 2010

Preparation of a transparent electrode using a poly-carboxylic multi-walled carbon nanotube; Shigeaki Abe, Katsutoshi Nakayama, Daisuke Hayashi, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, Tomoya Takada, 9th International Conference on Nano-Molecular Electronics, Kobe, Dec. 2010

Facilities and Capabilities

XSAM: HORIBA XGT2000V, Scanning Xray 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 P4010, ICP emission spectrometer for analysis of elements in

aquaous solution
FT/IR : Jasco FT/IR300E, FT/IR spectrometer with microscopic IR measurement
Particle Size Analyzer : Shimadzu SALD7000, 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, NdYAG pulse laser welder with computer controlled xy 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

LABORATORY OF ADVANCED HIGH-TEMPERATURE 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, oxidation of metals such as superalloys, intermetallic compounds, iron-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 $\alpha-\gamma$ 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) Water vapor effects on the high temperature oxidation of Ni-Al based Al_2O_3 forming alloys

The effects of water vapor on the oxidation of γ'-Ni-25 at% Al-Pt alloys are still being investigated. Water vapor increased the initial oxidation mass gain on the low Pt containing alloys, but no effect was observed on the exclusive Al_2O_3 forming high Pt containing alloys. For a longer-term oxidation, growth rate of α-Al_2O_3 scale was found to decrease with water vapor present. However it was found that water vapor stabilized metastable Al_2O_3 for a longer time exposure, and the metastable Al_2O_3 grains grew significantly larger with water vapor present.

(5) Phase transformation behavior of Al_2O_3 scale during high temperature oxidation

Very thin (~50 nm) Fe, Cr, or Ti coating on NiAl or FeAl alloys was found to suppress formation of metastable Al_2O_3, α-Al_2O_3 scale formed from the initial stage of oxidation, and the growth rate of coated alloy decreased significantly. In-situ X-ray diffraction measurement by Synchrotron radiation, confirmed that α-Al_2O_3 phase nucleated from initially formed Fe_2O_3, indicating that the “sympathetic nucleation” of α-Al_2O_3 scale from the corundum crystal of Fe_2O_3 occurred. It was also found that Ni-coating was stabilized metastable Al_2O_3 which has spinel structure, and, therefore, retard the phase transformation to α-Al_2O_3 scale.

(6) Effect of oxygen content on the stability of an Al_2O_3 scale on Nb(O)-Al-X alloys

The formation behavior of an Al_2O_3 scale on Nb(O)-Al-X alloys are being investigated. Oxygen content in Nb substrate was changed with the addition of Re, Mo, and Ta. The formation behavior of an Al_2O_3 scale on the oxygen saturated Nb(O)-X was conducted by an Al pack-cementation process. A very thin, well adhesive Al_2O_3 scale was found to develop on the alloy with higher oxygen content, but formation of a Nb-aluminide + internal Al_2O_3 mixture layer was observed on the alloy with intermediate oxygen content. Only the Nb-aluminide layers were formed on the alloy with low oxygen content. Using of oxygen as a alloying element for Nb alloys is now under investigating to develop the Nb(O) based Al_2O_3 forming alloys.

(7) Phase transformation behavior of thermally grown FeO on pure-Fe and Fe-Mn alloys

Isothermal phase transformation behavior of FeO, which formed on Fe or Fe-Mn alloys at higher temperature in air is being investigated. At higher temperature around 500°C, outer Fe_3O_4, which formed during an oxidation, grew inwardly during the phase transformation and Fe_3O_4 layer formed at scale/substrate interface. At the end of phase transformation FeO, which was sandwiched between an outer and an inner Fe_3O_4, finally transformed to eutectoid Fe_3O_4+Fe. It was found that the increase in Fe content in FeO due to a rejection of Fe by the growth of outer Fe_3O_4 caused Fe supersaturation in FeO, resulting the eutectoid phase transformation.

(8) Effect of water vapor on the oxidation of pure-Ni

The effect of water vapor on the oxidation of pure-Ni is being investigated. Water vapor was found to have little effect on the oxidation mass change of pure-Ni. However, a duplex oxide layer with outer very porous and inner dense NiO was formed when a pure-Ni was oxidized in an atmospheres containing water vapor. The formation of outer porous layer was not affected by oxygen content in the atmosphere, but greatly be affected by water vapor content. The formation mechanism of the powder-like NiO layer is still being consideration.

Presentations

Liquid Phase Bonding of 9CrODS Ferritic Steelby using ODS Steel Insert Metal: H. Noto, S. Hayashi and S. Ukai: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan.,2010

High-Temperature Deformation Mechanism of ODS ferritic Steels: 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., Sapporo, Jan.,2010

High-Temperature Deformation Mechanism of ODS ferritic Steels: Y. Sugino, S. Hayashi, S. Ukai, T. Kaito and S. Ohtsuka: The Spring Meeting of Jpn. Inst. Metals., Tsukuba, Japan, Mar.,2010.

Liquid Phase Bonding of 9CrODS Ferritic Steelby using ODS Steel Insert Metal: H. Noto, S. Hayashi and S. Ukai: The Spring Meeting of Jpn. Inst. Metals., Tsukuba, Japan, Mar.,2010.

Effects of Tramp-Elements on High-Temperature Oxidation Scale in Fe: S. Kasahara, S. Hayashi and S. Ukai: The Spring Meeting of Jpn. Inst. Metals., Tsukuba, Japan, Mar.,2010.

High-Temperature and Long-Term Oxidation Behavior of γ'-Ni-25Al-10Pt alloy under Steam Environment: M. Auchi, S. Hayashi, T. Narita and S. Ukai: The Spring Meeting of Jpn. Inst. Metals., Tsukuba, Japan, Mar.,2010.

Improvement of High-Temperature Oxidation Resistance in Oxidation Resistant Alloys and Coating by earlier formation of α-Al_2O_3: S. Hayashi, Y. Kitajima, F. Stewart, T. Narita and S. Ukai: The Spring Meeting of Jpn. Inst. Metals., Tsukuba, Japan, Mar.,2010.

Cyclic High-Temperature Carbonization and Oxidation Behavior of Hastelloy-X Alloy: T. Matsukawa, S. Hayashi, S. Ukai and H. Yaquwa: The Spring Meeting of Jpn. Inst. Metals., Tsukuba, Japan, Mar.,2010.

Effects of Oxide Metals on Transient Liquid Phase Bonding: H. Noto, S. Hayashi and S.Ukai: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jul.,2010.

Grain Boundary Sliding of ODS Ferritic Steels: S. Sugino, 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., Sapporo, Jul.,2010.

Effect of Hf Addition and Grain Structure on the Mechanical Properties of Ni-based ODS Superalloys: Q. Tang, S. Ukai and S. Hayashi: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jul.,2010.

Relationship between Residual Ferrite and High-Temperature Strength in 9CrODS Ferritic Steels: R. Miyata, 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., Sapporo, Jul.,2010.

High-Temperature oxidation of pure Ni under Steam Environment: K. Toyota, S. Hayashi and S. Ukai: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jul.,2010.

Stability of Oxide Particles in Austenitic ODS Steel under Iron irradiation: Y. Yamazaki, H. Oka, C. Liu, H. Kinoshita, N. Hashimoto, S. Ohnuki and S. Ukai: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jul.,2010.

Microstructure Control of Co-base ODS Alloys: K. Takezawa, S. Hayashi and S. Ukai: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jul.,2010.

Development of Fast Reactor Core Materials and Role of Irradiation Test: S. Ukai and S. Ohtsuka: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Al_2O_3 Scale Formation on Ni-Low Al Alloy by Element Coating Method: T. Nii, S. Hayashi and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Acceleration of α-Al_2O_3 Formation on Ni-50%Al at 1150℃ Using Nano Metallic Coating: A. Shaaban, S. hayashi and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Effect of Fe Coating on Earlier Formation of α-Al_2O_3 Scale: Y. Kitajima, S. Hayashi, T. Nishimoto, T. Narita and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Effect of Steam Environment on θ-Al_2O_3 Oxidation Scale in Ni-25Al-10Pt Alloy: M. Auchi, S. Hayashi, T. Narita and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Cold-Rolling and Recrystallization Characteristic in 12CrODS Ferritic Steel: T.

Narita, S. Ukai, B. Leng, S. Ohtsuka and T. Kaito: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Grain Boundary Sliding of ODS Ferritic Steels: S. Sugino, S. Hayashi, S. Ukai, T. Kaito and S. Ohtsuka: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Recrstallization Texture of Cold-Rolled ODS Ferritic Steel Annealing at Different Temperature: B. Leng, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Effects of Oxide Metals on Transient Liquid Phase Bonding: H. Noto, S. Hayashi and S.Ukai: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Relationship between Residual Ferrite and High-Temperature Strength in 9CrODS Ferritic Steels: R. Miyata, S. Hayashi, S. Ukai. T. Kaito and S. Ohtsuka: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Stability of Oxide Particles in Austenitic ODS Steel under Iron irradiation: Y. Yamazaki, H. Oka, C. Liu, H. Kinoshita, N. Hashimoto, S. Ohnuki and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Effect of P Addition on Oxide Scale Formation and Adherence in Fe-Low P Alloys: S. Kasahara, S. Hayashi, S. Ukai, K. Honda, Y. Kondo and K. Yanagihara: The Autumn Meeting of Jpn. Inst. Metals, Sapporo, Japan, Sep., 2010.

Compositional and Environmental Effects on the Transformation of Metastable to Stable Al2O3 Scale: S. Hayashi, I. Saeki, T. Doi, Y. Nishiyama, S. Kyo, M. Segawa, and M. Sato, International Symposium on High-temperature Oxidation and Corrosion, Zushi, Japan, November, 2010.

Evolution of Al_2O_3 Scale Formed on Ni-Al-Pt Alloy in Atmospheres Containing Water Vapor: M. Auchi, S. Hayashi, T. Narita, and S. Ukai, International Symposium on High-temperature Oxidation and Corrosion, Zushi, Japan, November, 2010.

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Prof. T. Yonezawa ran the second year as the full professor in this laboratory. Mr. T. Tsukamoto helps us to explore NEDO program. Ms. M. Matsumoto, Mr. T. Narushima, and Ms. M. Sugawara joined this group and also worked for NEDO program. T. Narushima became a TEM technician. Dr. A. Hyono quitted our group at the end of October 2010 and began his academic carrier at Ohtsuka Lab. (Research group of Environmental Materials), Division of Materials Science and Engineering, Hokkaido University.

The research activities of this group are directed to the development of nanoparticle preparation processes, an understanding of the mechanism of the high temperature corrosion in super alloys, inter-metallic compounds and iron-based alloys, and to the development of the corrosion resistant alloys and corrosion protection of steels with a hot dipping method in sea-water front environment.

Heating *in-situ* TEM observation is also our research target. The research activity is also directed to an understanding of the solidification mechanism of metals and alloys.

Current topics on research are in the following:

(1) Copper Particle Synthesis and Application

Preparation and application of metallic copper fine and nanoparticles are carried out intensively. From copper oxides (CuO and Cu_2O), non-oxidized metallic copper nanoparticles are successfully prepared by a chemical reduction procedure. Thanks to the optimized covering organic polymer materials, copper particles are not readily oxidized and can be kept in powder form under ambient condition for several months. We are now able to disperse these particles independently and prepare Cu particle pastes. These pastes can be used as a conductive paste.

(2) Liquid plasma to form nanomaterials

Chemical reduction process may be the most common preparative process of nanoparticles, nanorods, as well as nanoplates. However, the preparation solution/dispersion should contain metal source, stabilizers, as well as reducing reagents. Especially stabilizers and reducing reagents are often added large excess amount. On the contrary, energy, such as photo-energy, microwave, sonification are good candidates for chemical reduction energies for nanoparticle preparation. We have recently succeeded to prepare metal nanoparticles by microwave plasma in water. This process is a very rapid and easy process and metal-to-metal preparation is also possible according to very high energy of plasma. 0-valent metal nanoparticles, alloys, metal oxides, as well as composite metal oxides can be prepared by this plasma process.

(3) *In-situ* observation of nanomaterials in TEM at high temperature

In order to reveal the detailed structural changes of nanosized materials at high temperature were revealed by *in-situ* TEM observation. With a special gas introducing specimen folder, the sample can be heated up to 1500 °C. With such equipments, we observe the sintering process of copper nanoparticles or other particles, as well as the crystalling process of nanomaterials.

(4) Surface-assisted laser desorption/ionization mass spectroscopy

Mass spectroscopy is one of the most important chemical analyses especially understanding the structure of the unknown compounds. Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy is probably most important MS method in order to understand *m*/*z* values of synthetic polymers as well as biopolymers. This MS method is very easy and UV pulse laser was just irradiated to the mixture of the sample and organic matrix compounds for soft-ionization of the specimens. However, MALDI-MS method is not suitable for the mass analyses of organic molecules in relatively low mass range, *i.e.*, $m/z < 500$ because in this mass range, many mass peaks of the fragment ions of the organic matrix itself. The strength of the peaks of such ions is very strong compared to the sample ions. In order to overcome such problems, surface-assisted laser desorption/ionization (SALDI) mass spectroscopy has been intensively studied recently. Our laboratory provides various metal and inorganic nanoparticles for that purpose.

Presentations

Presentation titles are listed in our homepage:
http://labs.eng.hokudai.ac.jp/labo/limsa/?page_id=386

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S. Egawa, M. Yoshida, A. Nakagawa, A. Sado, T. Yamamoto and T. Uchiyama

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 especially at high temperatures. The wide variety of researching approach is introduced such as molten salt electrolysis, thermoelectric energy conversion, etc. 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 molten electrolysis of $CaCl_2$ 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 2011, and he began to study the micro- and nano-structure fabrication by electrochemical techniques such as molten salt at high temperature, anodizing, electrochemical etching, and electrodeposition.

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.

(2) Fabrication of nanoscale meniscus lenses by anodizing

A meniscus lens array with nanometer size range was fabricated by aluminum anodizing and electrochemical etching. Highly ordered pore array on aluminum can be obtained by anodizing in acidic solutions such as oxalic, sulfuric, and phosphoric acids. Anodizing in neutral borate solution after dissolution of porous type oxide film caused the formation of meniscus lens array of barrier type oxide film, and the shape of the lens array could be controlled by the potential and current density during anodizing.

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.

Prof. R.O. Suzuki was invited at the 5th Forum on New Materials (CIMTEC2010) which was held at Montecatini Terme, Italy, May 2010. He talked on the fluid dynamic simulation for thermoelectric energy conversion. Prof. R.O. Suzuki was invited at 2nd International Round Table on Titanium Production in Molten Salts which was held at Tromso and Trondheim, Norway, September 2010, and talked a keynote lecture on the recent studies on OS process. In domestic area, Prof. R.O. Suzuki made an invited memorial lecture at Molten Salt Committee

(Osaka, February) on electrochemical reduction of the oxides using molten chlorides when wining the annual Molten Salt Award.

Dr. Kikuchi attended 10th International Symposium on Biomimetic Materials Processing (BMMP-10) held in Nagoya, Japan, and he talked on “Fabrication of Micro-channels on Aluminum by Laser Irradiation and Electrochemical Techniques”

The following foreign scientists visited this laboratory: Dr. Molten Onsrud, Norwegian University of Science and Technology, Trondheim, Norway. Dr. R. Spolenak, ETH Zurich, Switzerland. Dr. G. Y. Sohn, Kyungpook National University, Korea. Dr. Anna Infortuna, RUAG Aerospace Defence Technology, Zurich, Switzerland. Prof. Dr. Urs Gonzenbach, ETH Zuerich, Switzerland.

Dr. Min Chen from Aalborg University, Denmark, studied with us as JSPS-research fellow from April to September. Mr. H.K. Sui joined us at October from Tongji University, Shanghai, China, as a master course student. Ms. Li Rongfua from University of Science and Technology Beijing (USTB) joined us as a special research student.

Presentations

Formation of granular Nb by calciothermic reduction of NbO; T. Satoh, M. Baba and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan. 2010.

Reduction of TiO in the molten $CaCl_2$; N. Kobayashi, K. Kobayashi and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan. 2010.

Carbon formation from CO_2 gas using molten salt electrolysis in $LiCl-L_2O$; K. Otake, H. Sakai, H. Kinoshita and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Chem. Soc., Sapporo, Jan. 2010.

Fabrication of Micro-channels on Aluminum by Laser Irradiation and Electrochemical Techniques; T. Kikuchi, Y. Wachi, M. Sakairi, T. Yonezawa, and

H. Takahashi : 10th International Symposium on Biomimetic Materials Processing, Nagoya, Jan. 2010.

Reduction of oxides using CaO electrolysis in molten calcium chloride, R.O.Suzuki, Annual Meeting of Molten Salt Committee 2010, Osaka, Feb., 2010.

Toughness of the film produced by high velocity flame injection, K.Watanabe, H. Kinoshita, R.O. Suzuki, T. Nakamura, Annual Meeting of Jpn. Inst. Metals, Tsukuba, March 2010.

Electrodeposition on Polypyrrole Electrodes; T. Kikuchi, M. Ueda, M. Sakairi, and T. Yonezawa : The 121th Annual Meeting of Surf. Finsh. Soc. Jpn., Tokyo, March 2010.

Power generation using the fluid blowing perpendicular to the TE panel, Y. Sasaki, M. Chen, and R.O. Suzuki, Int. Conf. of Thermoelctrics (ICT2010), Shanghai, China, June 2010.

System-level modelling of thermoelectric generation in a circuit simulator, M. Chen, L.A. Rosendahl, J. Zhang, J. Zhu, J. Gao, and R. O. Suzuki, Int. Conf. of Thermoelctrics (ICT2010), Shanghai, China, June 2010.

Optimal fluid Direction in the paths among thermoelectric multi-panels, R. O. Suzuki and Y. Sasaki, Int. Conf. of Thermoelctrics (ICT2010), Shanghai, China, June 2010.

Multi-Layered thermoelectric power generator, R.O. Suzuki, 5th Forum on New Materials (CIMTEC2010), Motecatini Terme, Italy, June 2010.

Microstructure Fabrication by Laser Irradiation and Electrochemical Techniques; T. Kikuchi : 2010 Summer Seminar of the Hokkaido Sections of Surf. Finsh. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sprroro, July 2010.

Simulation of thermoelectric power generation when the fluids are blown perpendicularly to the panels, Y. Sasaki, R.O. Suzuki and M. Chen., 7th annual meeting of Jpn. Thermoelectric Society, Y. Sasaki, R.O. Suzuki and M. Chen, 7th Annual Meetng of Jpn. Thermoelectric Soc., Tokyo, Aug., 2010.

Computational Modeling of the Thermal Regime of Thermoelectric Generators in Marine Power Plants, M.Chen, Y. Sasaki and R.O. Suzuki, 7th Annual Meetng of Jpn. Thermoelectric Soc., Tokyo, Aug., 2010.

Electrolysis and reduction of CO_2 gas in molten salt using ZrO_2 solid state electrolyte, K. Otake, H. Sakai, H. Kinoshita, T. Kikuchi and R.O. Suzuki, Annual meeting of Jpn. Electrochem. Soc., Atsugi, Sep., 2010.

Electrolysis of $CaCl_2$-CaO, D. Yamada, T. Kikuchi and R.O. Suzuki, Annual meeting of Jpn. Electrochem. Soc., Atsugi, Sep., 2010.

Nickel oxide electro-reduction in Molten $CaCl_2$+CaO, R. F. Descallar, N. Kobayashi, S. Osaki, T. Kikuchi, R.O. Suzuki, Annual meeting of Jpn. Electrochem. Soc., Atsugi, Sep., 2010.

Fabrication of Alumina Microlens array; T. Kikuchi, Y. Wachi, M. Sakairi, T. Yonezawa, and R. O. Suzuki : Annual meeting of Jpn. Electrochem. Soc., Atsugi, Sep., 2010.

Fundamental Study on Molten $CaCl_2$-CaO, D. Yamada, Y. Oka, T. Kikuchi, R.O. Suzuki, The 42nd Symposium on Molten Salt Chemistry, Hakodate, Sep., 2010.

Carbon production by electro-reduction from CO_2 gas in molten salt, K. Otake, H. Sakai, H. Kinoshita, T. Kikuchi, and R.O. Suzuki, The 42nd Symposium on Molten Salt Chemistry, Hakodate, Sep., 2010.

Reduction behavior of TiO and $CaTiO_3$ in $CaCl_2$+CaO molten salt, N. Kobayashi, K. Kobayashi, T. Kikuchi and R.O. Suzuki, The 42nd Symposium on Molten Salt Chemistry, Hakodate, Sep., 2010.

Electrochemical reduction of NiO in Molten $CaCl_2$+CaO, R.F.A. Descallar, S. Osaki, N. Kobayashi, T. Kikuchi, R.O. Suzuki, The 42nd Symposium on Molten

Salt Chemistry, Hakodate, Sep., 2010.

Current activities of OS process using molten CaO+$CaCl_2$, R.O. Suzuki, 2nd Intern. Round Table on Titanium Production in Molten Salts, Tromso-Trondheim, Norway, Sep., 2010.

Ca formation by electrolysis of $CaCl_2$-CaO melt, D. Yamada, T. Kikuchi and R.O. Suzuki, 147th annual meeting of Jpn. Inst. Metals, Sapporo, Sep., 2010.

Reduction of TiO in the $CaCl_2$ melt, N. Kobayashi, K. Kobayashi, T. kikuchi and R.O. Suzuki, 147th annual meeting of Jpn. Inst. Metals, Sapporo, Sep., 2010.

Nickel powder production directly from nickel oxide in molten $CaCl_2$, R.F.A. Descallar, S. Osaki, N. Kobayashi, T. Kikuchi, R.O. Suzuki, 147th annual meeting of Jpn. Inst. Metals, Sapporo, Sep., 2010.

Carbon preparation from CO_2 gas by electrolysis of molten salt LiCl-Li_2O, K. Otake, H. Sakai, H. Kinoshita, T. Kikuchi and R.O. Suzuki, 147th annual meeting of Jpn. Inst. Metals, Sapporo, Sep., 2010.

Simulation of Thermoelectric power generation when the fluids are perpendicularly blown to the panel, Y. Sasaki, R.O. Suzuki and M. Chen, 147th annual meeting of Jpn. Inst. Metals, Sapporo, Sep., 2010.

Fabrication of Micro-Channels on Aluminum by Laser Irradiation and Electropolishing; T. Kikuchi, M. Ueda, M. Sakairi, and T. Yonezawa : The 122th Annual Meeting of Surf. Finsh. Soc. Jpn., Sendai, Sep. 2010.

Multi-layered thermoelectric power generator, R.O.Suzuki, JST-MOST Project & CREST-Koumoto Team Joint Workshop, Sapporo, Oct., 2010.

Radiation in solar TE power generation, T. Fujisaka, Y. Sasaki, R.O. Suzuki, JST-MOST Project & CREST-Koumoto Team Joint Workshop, Sapporo, Oct., 2010.

Simulations of flat panel thermoelectric power generation systems using thermal fluids, Y. Sasaki, M. Chen, R.O. Suzuki, JST-MOST Project & CREST-Koumoto Team Joint Workshop, Sapporo, Oct., 2010.

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. 5 mass%-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. 6 mass%-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.50 V and 20 A.
High voltage amplifier: Takasago Electrics. 100 V-8000 V.
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 1500 C.
Thermal Conductivity Measuring Unit: Kyoto Electrics. Hot disk method at room temperature.

ADVANCED COATING LABORATORY

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Dr. T. Izumi (Hitachi Co. Ltd.)
Mr.S. Harashima (Nittobo Co. Ltd.)

The Specially Promoted Research (2006-2010) supported by Japanese Government has been finished by end of March, 2010. A new laboratory was established on advanced coatings, supported by Nittobo Co. Ltd., for term of three years (2010/07~2012/06), focusing on research and development of novel diffusion barrier coating systems to improve high temperature capabilities of ultra high temperature materials.

This research projects are aiming to transfer our research successes to the practical uses, such as gas turbines and jet engines. Current topics on research are in the following:

1) R & D of novel DBC systems to refractory metals such as Nb, Mo, and W.

2) Application of the DBC system to Ni base SC superalloy for land base gas turbines,
3) Application of the DBC system to Ni-based alloys and Fe-based alloys
4) Understanding high temperature oxidation and corrosion behavior of alloys and coatings.

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Our group has continued fundamental research in the field of corrosion science and engineering, development of corrosion monitoring system and equipment, surface finishing of aluminum and magnesium alloys and corrosion related phenomena in fuel cell. Current topics on research are in the following:

(1) Development of a new surface coating method 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. Since the direct prating of metals on Mg alloys is considerably difficult, zincate pretreatment was examined in order to replace the alloy surface with Zn thin layer. Zn particles deposited non-uniformly on AZ91D alloy because of non-uniform dissolution and corrosion on the α- phase and the β-phase surfaces due to their galvanic coupling. Such non-uniform deposition of Zn resulted in low coverage with Zn and thus low adhesivity of the plating layer to the substrate. Ultrasonic agitation at the initial stage of zincate process could improve slightly the uniformity of Zn deposition and adhesion strength.

(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 plant to be stored deep-underground to separate them from civil environment. Temperature-compensated resistometry method was applied to evaluate corrosion rate of copper in repository condition. A couple of Cu films with thickness of 5 μm was sealed in laminate film, and one of them was exposed to electrolyte solution containing various kinds of ions contained in underground water kept at 80°C. From the relative electric resistance change of Cu foil exposed to the solution against to the Cu foil protected from corrosion environment, actual corrosion loss of Cu foil surface was calculated in the accuracy of sub nm order. Corrosion was accelerated in the solution containing sulfide ions or chloride ions, while addition of carbonate ions suppressed proceeding of corrosion. Corrosion products formed on Cu foil was analyzed by using laser Raman spectroscopy and accumulation of Cu_2O on the corroded specimen and formation of basic copper carbonate such as $CuCO_3(OH)_2$ were confirmed.

(3) Development of miniature pH sensor for measurement of local pH

pH is an one of the dominant factor in many corrosion phenomena and thus measuring pH in the actual corroding system has been an important issue in the corrosion science. Application of pH sensor commercially available 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 and operation temperature. pH sensitive Ir oxide electrode with 0.2 mm in diameter was therefore prepared by using anodic electrodeposition and also 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. Both of electrodeposited IrOx and anodically oxidized IrOx electrodes showed good pH sensitivity. After long time immersion, however, electrodeposits of IrOx was partly detached from the electrode surface while anodically oxidized electrode maintained its pH sensitivity for long time. Further improvement of these electrodes is necessary for long time operation at high temperature.

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

High voltage more than 100 Vdc was applied to two electrodes immersed in KCl solution to form micro-plasma within the narrow gap placed in the solution between the electrodes. The gap was formed by making a small hole of 0.2 to 1.0 mm in diameter in a glass plate or a fused quartz plate. Micro-plasma was observed in the gap smaller than 0.7 mm in diameter due to concentration of polarization current and thus focusing the heat generation due to Ohmic loss in the solution. Temperature elevation of local electrolyte solution caused limited boiling and applying high voltage to the vapor phase ignited plasma formation. Spectra of light emitted from the micro-plasma was analyzed by using an optical fiber spectrometer and it was confirmed that the light contains atomic lines of ionic species contained in the solution. The wall of the narrow gap was gradually abraded by the high temperature plasma, resulting in widening the gap which lessened plasma intensity. Abrasion rate of the glass plate gap was considerably faster than that of quartz plate.

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

Many corrosion phenomena proceed in a non-uniform manner and coupling distribution 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 to apply to many corrosion system. For analysis of atmospheric corrosion of steel we developed a 100 channel electrode system and applied it to a specimen which was composed of 100 piece of iron rod embedded in resin exposed to wet and dry environment to measure the spatial distribution of the coupling current. After dropping a droplet of NaCl solution on the surface to initiate corrosion, galvanic couple was formed between electrodes in the corroding area. Coupling current increased in wetting cycle and decrease in drying cycle with some delay caused by preservation of water within the rust. The coupling current increased and coupling area became wide with proceeding corrosion and then ceased when the specimen surface was covered with thick rust. When the specimen was coated with acrylic paint small and narrow coupling current was observed under the paint.

Presentation

K. Azumi: Corrosion Measurement of Metals in Saltely Plant using Multichannel Electrodes Method, The 22nd Meeting of Research Grant of the Salt Science Research Fundation, July, 2010, Tokyo

T. Jinwei and K. Azumi: Optimization of pulsed electrodeposition of aluminum from $AlCl_3$-1-ethyl-3-methylimidazolium chloride ionic liquid, The 2nd Korea-Japan Joint Symposium ARS & Capacitor, Jun, 2010, Gyeongsangbuk-do, Korea

Y. Sato, K. Azumi: Fabrication and characterization of proton conducting pseudoboehmite thin film (Poster), ibid.

K. Azumi, A. Naganuma : Crevice corrosion monitoring of high-corrosion-resitive steels in the solution containing high concentration of sodium chroride at high temperature using multichannel electrode system, Symp. on "Analysis of Corrosion Mechanism and Development of Evaluation Technology in the Salt Production Industry" at the 61st meeting of Society of Sea Water Science, Japan, Jun (2010) Ishinomaki

K. Azumi: Measurement of Corrosion Rate of Cu Thin Foil in Aqueous Solution at High Temperature using Temperature-compensating Resistmetory, Annual meeting of Japan Society of Corrosion Engineering 2010, May, 2010, Tokyo

K. Azumi, J. Yajima: Evaluation of Copper Corrosion Rate in Underground Water at High Temperature Using Resistometry, 8th Spring Meeting ISE, May, 2010, Columbus Ohio, USA

K. Azumi, A. Naganuma: Measurement of Crevice Corrosion using Multichannnel Electrode Method, 77th Annual Meeting of Electrochemical Society of Japan, March, 2010, Toyama

T. Jinwei, K. Azumi: Effect of Pulse Form on Electrodeposition of Al in Ionic Solution at Room Temperature, ibid.

Y. Aoki, K. Azumi: Formation of Silver Thin Film using SIlver Mirror Reaction and Its application to Thin Ag/AgCl Reference Electrode, ibid.

Y. Sato, K. Azumi: Fabrication and Characterization of Proton Conducting Pseudoboehmite Thin Film, ibid.

J. Yajima, K. Fushumi, K. Azumi: Development of Electrochemical Dissolved Oxygen Sensor using a Carbon Microelectrode, ibid.

J. Kanno, K. Azumi: Effect of Additives on Ni Plating Film and Analysis of Their Adsorption Manner , Winter Joint Meeting of the Hokkaido Branch of the Chemistry Related Societies, Febrary, 2010, Sapporo

Y. Aoki, K. Azumi: Fabrication of Ag/AgCl Reference Electrode Formation using Silver Mirror Reaction, ibid.

Y. Sato, K. Azumi: Fabrication of Proton Conducting Pseudoboehmite Film, ibid.

J. Yajima, K. Fushumi, K. Azumi: Development of Dissolved Oxygen Sensor using Carbon Microelectrode Array, ibid.

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

Current topics on research are as follows:

(1) Application of Coaxial Double Ring Microelectrode to the Probe of a Scanning Electrochemical Microscope

The probe microelectrode for a scanning electrochemical microscope (SECM) is composed of a noble metal wire or carbon fiber sheathed in insulating glass or inorganic coating. However the fabrication of the smaller microelectrode was extremely difficult and sometimes expensive. The simple heating treatment with town gas in Sapporo was applied to form carbonaceous layers on both inside and outside of sharpened quartz capillaries. After the lead wiring and the partial insulating coating, double ring microelectrodes were successfully fabricated from the capillaries.

Electrochemistry in the solution containing redox mediator revealed that current flows on both inner and outer ring microelectrodes were interfered each other and the outer one could play a role of shielding electrode for the inner one as the double microelectrodes were used as the probe of SECM. Using a model specimen composed of platinum and epoxy resin, the performance of the probe was investigated. The sensitivity and lateral resolution of the tip current image in the SG/TC mode SECM were improved by 50% and 5%, respectively.

(2) Anisotropic dissolution of polycrystalline iron in sodium sulphate solution

It is important for well–understanding of basic corrosion phenomena to investigate the mechanism and kinetics of corrosion depending on crystallographic orientation of metal substrate. Anisotropic dissolution of a polycrystalline pure iron in sodium sulphate solution (pH 2.3) was investigated by using an SECM, in which the product of ferrous ions generated from the iron specimen was detected on the probe. The dissolution rate on 3 2 5 grain was larger than that on 0 0 1 grain. This behavior was different from the order of corrosion current found by the simple polarization of single crystal iron in surpharic acid (pH 1). However, the contradiction could be explained by the anisotropic coverage and/or bonding energy of H on Fe at potentials around corrosion potential.

(3) Micro-indentation for Fabrication of Multi-microelectrode Array

The microelectrode has a number of benefits as an electrochemical sensor but flow a significantly weak current. In order to fabricate a microelectrode array, which is capable to flow a larger current than single microelectrode, a so-called micro-indentation technique has been applied. The micro-indentation of the anodized titanium surface was carried out in nickel electroplating bath to form partial electro-active areas. Cathodic polarization during the indentation allowed to deposit nickel not only on indents but also on sturdy passive surface. However, nickel could also be deposited in the indent during the indentation at open circuit potential. After this substitution of nickel with substrate titanium, the indents could be filled by nickel with the nickel electroless plating. The size and inter-distance of deposited nickel are capable to design by conditions of the indentation and electroless plating.

(4) Modification of Flowing-electrolyte Type Micro-droplet-cell

Flowing-electrolyte type micro-droplet-cell (f-MDC) developed for the micro-electrochemistry was modified to improve the stability of current flowing in the cell, the facility of the cell fabrication, and the lateral resolution in the scanning MDC application. Instead of a coaxial double capillary used in the conventional f-MDC, a multi-channel capillary, that was composed of an inner channel and six outer cannels for the supply fresh electrolyte and for the remove used electrolyte, respectively, was developed and applied to probe the local electrochemical reactivity on the aluminum alloys to fabricate the microstructure on the titanium.

Other Activities

In May, Dr. Koji Fushimi attended to 8th International Society of the Electrochemistry Spring Meeting held in Columbus, OH, and presented the paper entitled “Mechano-electrochemistry of passive surface using *in situ* micro-indentation test”. In September, Dr. K. Fushimi attended to 2010 European Materials Research Society Fall Meeting held in Warsaw, Poland, and presented the paper entitled “Carbonaceous Coating Electrodes Fabricated by Simple Heat Treatment”. Dr. K. Fushimi also attended to Electrochemical Micro. and Nanosystem Technology 2010 held in Cannes-Mandelieu, France, and presented the paper entitled “Dual-microelectrode for high resolution imaging of SG/TC mode SECM”. In October, Mr. Ken-ichiro Matsushita and Dr. K. Fushimi attended to Nagoya Univ.–Tsinghua Univ.–Toyota Motor Corp.–Hokkaido Univ. Joint Symposium—Materials Science and Nanotechnology for the 21st Century— held in Sapporo, Japan and presented the paper entitled “*In-situ* Interface Imaging with a Coaxial Double–Ring Microelectrode Probe in SG/TC Mode SECM”. Dr. K. Fushimi also attended to 218th Electrochemical Society Meeting held in Las Vegas, NV, and presented the paper entitled “*In-situ* Interface Imaging with a Shielded Probe in SG/TC Mode SECM”.

Presentations (international symposia)

K. Fushimi, T. Yamamoto, H. Habazaki, H. Konno, M. Seo; “Mechano-electrochemistry of passive surface using *in situ* micro-indentation test”, 8th Spring Meeting of the International Society of Electrochemistry, May 1-5, Columbus, OH (2010).

T. Murata, Y. Goto, M. Sakairi, K. Fushimi, T. Kikuchi; “Area selected anodic oxide film formation on Al by solution flow type micro-droplet cell”, The 2nd Korea-Japan Joint Symposium ARS&Capacitor, Jun. 27-28, Gyeongju, Korea (2010).

K. Fushimi, A. Ono, K. Matsushita, Y. Hasegawa, H. Konno; “Carbonaceous

Coating Electrodes Fabricated by Simple Heat Treatment", 2010 E-MRS Fall Meeting, Sep. 13-17, Warsaw, Poland (2010).

K. Fushimi, K. Matsushita, H. Konno, Y. Hasegawa; "Dual-microelectrode for high resolution imaging of SG/TC mode SECM", EMNT 2010, Sep. 21-24, Cannes-Mandelieu, France (2010).

K. Matsushita, K. Fushimi, Y. Hasegawa; "*In-situ* Interface Imaging with a Coaxial Double–Ring Microelectrode Probe in SG/TC Mode SECM", Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. Joint Symposium —Materials Science and Nanotechnology for the 21st Century—, Oct. 7-9, Sapporo, Japan (2010).

K. Fushimi, K. Matsushita, Y. Hasegawa, H. Konno; "*In-situ* Interface Imaging with a Shielded Probe in SG/TC Mode SECM", 218th ECS Meeting, Oct. 10-15, Las Vegas, NV (2010).

M. Sakairi, T. Murata, Y. Goto, K. Fushimi, T. Kikuchi; "Area Selective Formation of Porous Type Aluminum Anodic Oxide Film by Sf-MDC", 218th ECS Meeting, Oct. 10-15, Las Vegas, NV (2010).

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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 corrosion generated hydrogen, and 5) applied to anodizing and laser technique for micro-fabrication area.

The topics of investigation are in the following:

(1) Hydrophobic alumina film and its corrosion resistance

A porous type anodic oxide film was formed on aluminum with anodizing, and hydrophobicity of this film was developed by a simple and effective desiccation treatment. It was found that desiccation temperature does not influence contact angle, CA, greatly. From SEM and XPS observation, the hydrophobic layer shows a regular porous layer, with little change in surface chemical composition before and after the desiccation treatment. According to the interface model, water-arc in micro-pores would play the main role to increase CA. The rest potential in NaCl solution shows an order: Hydrophobic sample > anodized sample > electropolished sample, which accounts for the corrosion resistance improvement of both anodizing and desiccation treatment. The interface area between solution and aluminum is reduced as the air-valley phenomenon, which may be the reason for the improved corrosion resistance.

(2) Corrosion resistant titanium dioxide film formed on Mg by liquid phase deposition treatment

Liquid Phase Deposition treatment (LPD) was applied to form a corrosion protective titanium dioxide film on magnesium. Combination of solution pH control and addition of sucrose, it becomes possible to form a highly adhesive and thin titanium dioxide film on magnesium. The role of the sucrose may be attributed to the formation of tetrafluoroboric acid $(BF_4)^-$ in the solution reducing the homogeneous nucleation of titanium dioxide 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.

(3) High capacitance titanium dioxide 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. Combination of solution pH control and addition of sucrose, it becomes possible to form a highly adhesive and thin titanium dioxide film on aluminum. The post anodizing treatment formed TiO_2/Al_2O_3 composite layer, which shows very high capacitance more than 200% higher than that of anodized Al_2O_3 layer formed on electro-polished aluminum.

(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 locally on aluminum. This technique makes it possible to form anodic oxide film locally, and the thickness increases with number of repetition number of cell scanning. The substrate temperature shows important roll on film growth rate, high temperature of the specimen shows oxide film growth rate without any change of pore diameter. Using this technique, it is also possible 3D oxide film structure and micro-trench on the aluminum.

(5) Electrochemical behavior of 13Cr stainless steel in simulated oilfield environments

The effects of concentration of CH_3COONa, temperature and deaearation on electrochemical behavior such as pitting potential, rest potential and electrochemical noise data of low C - 13% Cr stainless steel were examined. Current change at constant potential, effect of stress and effect of H_2S concentration were also conducted to confirm availability of noise analysis technique in simulated oil and gas environments. In all solutions, both pitting and rest potential decrease with increasing solution temperature. The pitting potential of aerated samples is lower than that of deareated samples at higher temperature. The rest potential changes negative direction by deaeration. The passive current density (steady value of polarization curves) in deaerated solutions increases with increasing temperature, and the increasing rate is depended on concentration of CH_3COONa. The value of PSD of rest potential spectrum decreases with time and then increases again, while changes of rest potential shows no difference in time domain. This result suggests continuous noise analysis with FFT has an ability to measure susceptibility of pitting corrosion or difference in corrosion resistance with immersion time.

(6) Corrosion of 3003 Al alloy in model tap water

An influence of cations .such as magnesium ions in model tap water on corrosion behavior of A3003 was examined by immersion corrosion tests and galvanic corrosion tests. The potential fluctuations and current fluctuations observed while galvanic corrosion tests show good correlation. From the galvanic current, single existence of magnesium ions act as inhibitor, however, coexistence of magnesium ions and sodium ions accelerate of corrosion.

(7) Development of μ-electrochemical technique for detection of permeated hydrogen generated by wet-dry cycle

Permeated hydrogen shows very important role in hydrogen embrittlement, however, traditional electrochemical cell technique is not suitable for detection of hydrogen generated at damaged are of coated layer. A small size cell which has 0.3 cm^3 volume of detection side was successfully developed. The permeation current, amplitude about 10 nA, increases with increasing formed defect area and shows good reproducibility.

(8) Local Oxide Film Formation on Aluminum by Laser Irradiation and Anodizing with Ematal Bath

A new technique for fabrication of μ-circuit board made of aluminum and its oxide is established. This technique is based on anodizing of aluminum in Ematal bath and laser irradiation technique.

Other activities

In May, Assoc. Prof. Sakairi attended 8th Spring Meeting of the International Society of Electrochemistry and presented a paper entitled "Repassivation Behavior of Titanium in Artificial Saliva Investigated with a Photon Rupture Method" and " Formation and corrosion behavior of artificial pit of 2024 aluminum alloy with PRM".

In June, Assoc. Prof. Sakairi, Mr. R. Fujita, Mr. T. Murata and Mr. S. Fujita attended The 2nd Korea-Japan Joint Symposium ARS & Capacitor in Koria and Mr. Murata presented a paper entitled "Area selected anodic oxide film formation on Al by solution flow type micro-droplet cell", Mr. R. Fujita presented a paper entitled "Formation of Al_2O_3 Nano-dots with LPD and Anodizing", and Mr. S. Fujita presented a paper entitled "Localized oxide film formation on aluminum by laser irradiation and anodizing". Mr. Murata had a vest poser presentation award.

In September, Assoc. Prof. Sakairi and Mr. M. Zheng attended ICAA 12 at Yokohama and Mr. Zheng presented a paper entitled "Corrosion Resistance Improvement of Aluminum by Hydrophobic Anodic Oxide Film". Assoc. Prof. Sakairi and Mr. M. Zheng attended 5th ISMCC at Qingdao and Assoc. Prof. Sakairi presented a paper entitled "Corrosion Behavior of Titanium Oxide Coated Magnesium" and Mr. Zheng presented a paper entitled "Microstructure of Hydrophobic Alumina Film and it Corrosion Resistance Analysis". During the conference they visited Prof. Hou in Institute of Oceanology, Chinese Academy of Sciences.

In October, Assoc. Prof. Sakairi attended 218th annual meeting of ECS in Rasvegas, USA and presented a paper entitled "Area Selective Formation of Porous Type Aluminum Anodic Oxide Film by Sf-MDC". Assoc. Prof. Sakairi visited AGH University of Science and Technology, Krakow, Poland and attend AGH-HU symposium on international education.

Facilities

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

Fabrication of Micro-channels on Aluminum by laser Irradation and Electrochemical Techniques, T. Kikuchi, Y. Wachi, M. Sakairi, T. Yonezawa and H. Takahashi, BMMP-10, Nagoya, Jan. 2010.

Deposit of metals on PPy, T. Kikuchi, M. Ueda, M. Sakair, T. Yonezawa and H. Takahashi, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, Jan., 2010.

Line shape anodic oxide film formation on aluminum by Ematal Bath, S. Fujita, T. Kikuchi, M. Sakairi, T. Yonezawa and T. Takahashi, ibid.

Localized dissolution kinetics of model pit on 2024 aluminum alloy, K. Yanada, T. Kikuchi, M. Sakairi, Y. Oya, Y. Kojima, ibid.

Electrochemical measurements of stainless steel in high Cl^- solutions, J. Tatehara, M. Sakairi and T. Kikuchi, ibid.

Anodizing of micro-channel formed in sintered titanium, M. Ishida, T. Ohmi, M. Sakairi and M. Iguchi, ibid.

Repassibation behavior of Ti in artificial saliva -Effect of F^- -, M. Kinjyo, M. Sakairi and T. Kikuchi, ibid.

Local anodic oxide film formation on aluminum by Sf-MDC, Y. Goto, M. Sakari, T. Kikuchi and K. Fushimi, ibid.

Micro-machining on aluminum by laser irradiation and electrochemistry, Y. Wachi, T. Kikuchi, M. Sakairi, T. Yonezawa and H. Takahashi, ibid.

Structure change of Cu-Zn alloy by selective dissolution, K. Kobayashi, T. Ohmi, M. Sakari and M. Iguchi, ibid.

Local electrochemistry on metals by Sf-MDC, T. Murata, M. Sakairi, T. Kikuchi and K. Fushimi, Winter Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2010.

Corrosion protection of magnesium by LPD, R. Fujita, M. Sakairi and S. Nagata, ibid.

Corrosion of model cut-edge formed on coated steels -Effect of size-, M. Uchida and M. Sakairi, ibid.

Effect of cation on galvanic corrosion of aluminum in model tap water, K. Otani and M. Sakari, ibid.

Preparation and Corrosion Inhibitive Effect of Hydrophobic Anodic Oxide Film, M. Zhen and M. Sakairi, ibid.

Formation of aluminum anodic oxide film locally by Sf-MDC, Y. Goto, M. Sakairi, T. Kikuchi and K. Fushimi, 146th spring meeting of Jpn. Inst. Metals, Tokyo, March, 2010.

Effect of deposition conditions on electroplating by using PPy electrode, T. Kikuchi, M. Ueda, M. Sakairi and T. Yonezawa, ibid

Line type anodic oxide film formed on aluminum by laser irradiation, S. Fujita, T. Kikuchi, M. Sakairi, T. Yonezawa and H. Takahashi, ibid.

Analysis of structure of air formed oxide film on aluminum by synchrotoron X-ray, M. Sakairi, T. Suda, M. Sato and D. Nagasawa, The spring meeting of The Japan Institution of Metals, Tsukuba, March, 2010.

Electrochemistry of model interface by Sf-MDC, M. Sakairi, T. Murata and K. Fushimi, The Spring meeting of ISIJ, Tsukuba, March, 2010.

Micro patterning of metals by Sf-MDC, T. Murata, M. Sakariri, T. Kikuchi and K. Fushimi, The 77th Meeting of the Electrochem. Soc. of Jpn., Toyama, March, 2010.

Corrosion resistant TiO_2 film formed on magnesium by LPD, R. Fujita, M. Sakairi and S. Nagata, ibid.

Influence of Wettability on Corrosion Resistance of Anodized Aluminum in NaCl Solution, M. Zheng, M. Sakairi and T. Kikuchi, Ziryo-to-Kankyo 2010, Tokyo, May 2010.

Wet-dry corrosion behavior model scratch formed paint-coated steels, M. Sakairi, M. Uchida and T. Kikuchi, ibid.

Change of corrosion behavior of aluminum alloys by cations in model tap water, K. Otani, M. Sakairi and T. Kikuchi, ibid.

Rest potential measurement of model pit formed on 2024 Al alloy by laser machining, M. Sakairi, K. Yanada, Y. Otani and Y. Kojima, Spring meeting of Light metal soc., May, Osaka, 2010.

Repassivation Behavior of Ti in Artificial Saliva with PRM, M.Sakairi, M.Kinjyo and T. Kikuchi, ISE Spring Meeting, USA, May 2010.

Formation and corrosion behavior of artificial pit of 2024 aluminum alloy with PRM, M.Sakairi, K. Yanada, T. Kikuchi, Y. Oya and Y. Kojima, ISE Spring Meeting, USA, May 2010.

Area selected anodic oxide film formation on Al by solution flow type micro-droplet cell, T. Murata, Y. Goto, M. Sakairi, K. Fushimi and T. Kikuchi, The 2ndKorea-Japan Joint Symposium ARS & Capacitor, Korea, June, 2010.

Formation of Al_2O_3 Nano-dots with LPD and Anodizing, R. Fujita, M. Sakairi, H. Jha and T. Kikuchi, ibid.

Localized oxide film formation on aluminum by laser irradiation and anodizing, S. Fujita, T. Kikuchi and M. Sakairi, ibid.

Line shape anodic oxide structure formed on aluminum by Sf-MDC, T. Murata, M. Sakairi, K. Fushimi and T. Kikuchi, Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Hakodate, July, 2010.

Thin oxide film formation on metals by LPD, R. Fujita, M. Sakairi and T. Kikuchi, ibid.

Porous type anodic film formed on aluminum by Sf-MDC, T. Murata, M. Sakairi, T. Kikuchi and K. Fushimi, The 2010 autumn meeting of the Electrochem. Soc. of Jpn., Atsugi, Sept., 2010.

Formation of corrosion resistant oxide film on magnesium by LPD, R. Fujita, M. Sakairi and T. Kikuchi, ibid.

Effect of aluminum substrate temperature on porous type oxide film growth rate, M. Sakairi, T. Murata, K. Fushimi and T. Kikuchi, The 147th autumn meeting of Jpn. Inst. Metal, Sapporo, Sept., 2010.

Corrosion Resistance Improvement of Aluminum by Hydrophobic Anodic Oxide Film, M. Zheng, H. Jha and M. Sakairi, ICAA 12, Yokohama, Sep., 2010.

Corrosion Behavior of Titanium Oxide Coated Magnesium, M. Sakairi, R. Fujita, T. Kikuchi and S. Nagata, 5th ISMCC, Qingdao, Sept.,2010.

Microstructure of Hydrophobic Alumina Film and it Corrosion Resistance Analysis, M. Zheng, H. Jha, M. Sakairi and T. Kikuchi, ibid.

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Dealloying of Cu-Zn Microchannel Lining Layers for Producing Microporous Catalyst, K. Kobayashi, T. Ohmi, M. Sakairi and M. Iguchi, ibid.

Improvement of corrosion resistance of magnesium by LPD, M. Sakairi and R. Fujita, The 118th meeting of Light Metal Soc., Nagaoka, Nov., 2010.

Corrosion behavior of aluminum alloys in low Cl^- content water, K. Otani and M. Sakairi, The 27th ARS conf., Fujisawa, Nov. 2011.

Change in wettability of aluminum oxide film by heat treatment, M. Zheng and M. Sakairi, ibid.

The Influence of Desiccation Process on Wettability and Corrosion Behavior of Aluminum Oxide Film, M. Zheng and M. Sakair, Corrosion dream 2010, Tokyo, Dec., 2010.

Electrochemical detection of hydrogen formed by wet-dry corrosion tests of coated steels, S. Takagi and M. Sakairi, ibid.

ABSTRACTS of PUBLICATIONS

Protection of Steels with Conducting Polymer Coating

Toshiaki Ohtsuka
Bosei-Kanri, 2010, 223

Conducting polymer such as polyaniline (PANi), polypyrrole (PPy), and polythiophen (PThio) functions as an oxidative coating for steels and thus the steels coated by the polymer are easily passivated. The bilayerd PPy layer developed by the authors induces the passivation of the substrate steel for 190 hours in which no rusts are observed. The bilayered layer has a anti-corrosive property of self-healing.
(Japanese)

Self-Healing Ion-permselective Conducting Polymer Coating

D. Kowalski, M. Ueda, and T. Ohtsuka

Journal of Materials chemistry, **20**, 7630-7633 (2010)

The present work demonstrates a new approach to self-healing polymers that have the ability to repair artificial defects and restore the passive state of an underlying metal substrate. An intrinsically conducting polymer (ICP) with a well designed function of doped ions possesses specific permselective properties, restricting incorporation of aggressive chlorides from corrosive electrolyte. The cation permselective membrane controls the release of healing ions to the defect zone when artificial defects are formed, efficiently inhibiting corrosion of the underlying metal substrate.

Surface Finishing of Mg Alloys by Al Electroplating in $AlCl_3$-EMIC Ionic Liquid

Mikito Ueda, Yasushi Tabei, and Toshiaki Ohtsuka,
ECS Transactions, **33**, 563-570 (2010)

In order to improve the corrosion resistance of Mg and its alloys, Al layer was electrodeposited on their surface from aluminum chloride -1-ethyl-3-methylimidazolium chloride ionic liquid ($AlCl_3$-EMIC). Mirror-like Al surface can be electroplated in $AlCl_3$-EMIC ionic liquid by pulse electrolysis at 323 K, though Al layer was not dense and homogeneous. A dense and flat Al layer was successfully electroplated on Mg alloys in the $AlCl_3$-EMIC ionic liquid at lower temperature of 283 K.

Detailed Investigation of the Reduction Process of Cupric Oxide (CuO) to Form Metallic Copper Fine Particles with a Unique Diameter

Tetsu Yonezawa, Atsushi Hyono, Naoki Nishida

Journal of Materials Science, **45**, 6433–6439 (2010)

Copper fine particles were successfully prepared by hydrazine reduction of cupric oxide (CuO). Changes in the temperature and pH values during the redox reaction of cupric oxide and hydrazine monohydrate were observed in detail. These changes reflected the reaction steps leading to the formation of metallic copper particles. The reduction of cupric oxide proceeded mainly during the part of the process where the pH value changes little or only very slowly. This phenomenon strongly indicates that the reaction and the particle structures can be established by control of the pH during the formation.

Preparation of Zinc Oxide Nanoparticles by Using Microwave-induced Plasma in Liquid

Tetsu Yonezawa, Atsushi Hyono, Susumu Sato, Osamu Ariyada

Chemistry Letters, **39**, 783-785 (2010)

As a rapid and easy liquid process for preparation of ZnO nanoparticles, we propose here a microwave-induced plasma in water. Generation of plasma in liquid has been achieved at atmospheric pressure without external gas bubbling. After only several minutes of microwave irradiation, about 0.3 g of ZnO nanoparticles was obtained from an aqueous solution of zinc(II) acetate under alkaline conditions.

One-pot Preparation of Antioxidized Copper Fine Particles with a Unique Structureby Chemical Reduction at Room Temperature

Tetsu Yonezawa, Naoki Nishida, Atsushi Hyono

Chemistry Letters, 39, 6, 548-549 (2010)

A one-pot and single-step reduction process for producing antioxidized copper fine particles will be described. This process can be carried out at room temperature, and size range is quite wide, from 190 nm to 1 μm by varying the amount of gelatin, the stabilizing reagent. From SEM images it is revealed that higher loading of gelatin gave larger but relatively uniform particles. However, XRD patterns indicated that the large particles were composed of smaller particles; that is, they had a “particle-in-particle” structure. Cross-sectional TEM image strongly supports this structure and indicates that gelatin is a good antioxidizing coating material which kept 5-nm copper metallic.

Ion-Conducting, Sub-100 nm-thick Film of Amorphous Hafnium Silicate

Y. Aoki, H. Habazaki and T. Kunitake

Solid State Ionics, **181**, 115-121 (2010)

Ceramic electrolytes operating in the temperature range of 200 to 500ºC under dry atmosphere are a key material for the next-generation fuel cell and related applications. We discovered that nanometer-thick films of amorphous hafnium silicate ($Hf_nSi_{1-n}O_x$) exhibited efficient ionic conduction at 100-400ºC in dry air. When the fraction of hafnium doping was around 0.1, the nanofilm showed a low area-specific-resistance ($<0.15\ \Omega\ cm^2$) at around 350 ºC that was small enough for the practical fuel cell application. The sub-100 nm-thick membranes of $Hf_{0.13}Si_{0.87}O_x$, could be fabricated on porous Pt/alumina substrate to provide gas concentration cells. The electromotive force observed with H_2 concentration cell indicated that the ceramic nanomembrane acted as predominant proton conductor without permeation of H_2 gas. In addition, the $Hf_{0.13}Si_{0.87}O_x$ and $Zr_{0.11}Si_{0.89}O_x$ membranes responded to the change of O_2 pressures in O_2 concentration cells, while the $Al_{0.16}Si_{0.84}O_x$ and $Ce_{0.06}Si_{0.94}O_x$ membranes did not produce the electrical voltage by gradient of O_2 pressure. We conclude that $Hf_{0.13}Si_{0.87}O_x$ nanomembrane is promising as electrolyte material for fuel cells and related ionics devices.

Thickness-induced Proton-conductivity Transition in Amorphous Zirconium Phosphate Thin Films

Y. Aoki, K. Ogawa, H. Habazaki, T. Kunitake, Y.Z. Li, S. Nagata and S. Yamaguchi

Chemistry of Materials, **22**, 5528-5536 (2010)

Amorphous zirconium phosphate thin films, a-$ZrP_{2.5}O_x$, revealed unique proton conductivity transition induced by reducing thickness due to the formation of highly conductive, hydrated nanolayer. The dense films made of a metaphosphate glass phase were uniformly formed over the electrode substrate by multiple spin-coating with a mixed precursor sol, as checked by TEM and RBS. When thickness d was larger than 60 nm, the proton conductivity across film and the activation energy E_a were not variable with d. σ abruptly increased 200 times and E_a decreases from 0,9 to 0.7 eV when d decreased from 60 to 40 nm. and it became thickness-independent again in $d < 40$ nm. E_a of 100 mm-thick film is increased to the similar value as that of the 40 nm thick by annealing at 400ºC in H_2O/air. It was concluded that the conductivity transition could be associated with the hydration of metaphosphate nanolayer. The hydrated, high-conductive phase was very stable only when the thickness was less than 100 nm. Therefore, the films of more than hundreds nm thickness cannot change to the high-conducting hydrated phase throughout the film thickness. These unprecedented behaviors could not be explicable with a simple model based on the core space charge or continuum structural relaxation at hetrointerface.

Controlled Morphology of Aluminum Alloy Nanopillar Films: From Nanohorns to Nanoplates

T. Fujii, Y. Aoki, K. Fushimi, T. Makino, S. Ono and H. Habazaki

Nanotechnology, **21**, 395302 (2010)

Nanopillar films of Al-Nb alloys have been fabricated on substrates with a regular concave cell structure by oblique angle physical vapor deposition. The concave cell structure of the substrate increases the shadow region for the flux of depositing atoms, assisting the formation of an isolated nanopillar on each cell. Depending upon the alloy composition and deposition angle, the pillar shape changes from horn-like nanopillars through triangular nanoprisms to nanoplates. The Al-Nb alloy nanoplate films with wide gaps between plates are of interest as electrodes for capacitor applications. The dielectric oxide film formed on the nanoplate film showed a capacitance more than ten times larger than that on the respective flat film, due to the enlarged surface area.

Tracer Studies Relating to Alloying Element Behaviour in Porous Anodic Alumina Formed in Phosphoric Acid

S.J. Garcia-Vergara, H. Habazaki, P. Skeldon and G.E. Thompson

Electrochimica Acta, **55**, 3175-3184 (2010)

The behaviours of hafnium, molybdenum and hafnium tracer species in porous anodic alumina films are compared in order to investigate the relationship between the migration rate of alloying element species and their amounts and distributions in the films. The study employs substrates consisting of a thin layer of Al-Hf, Al-Mo or Al-Nd alloy deposited by magnetron sputtering on to electropolished aluminium, with a top layer of aluminium deposited above the alloy layer. The substrates are then anodized at constant current density in phosphoric acid to incorporate the tracer species into the porous anodic film. The tracer distributions in the film are investigated by scanning electron microscopy, and the amounts of tracer quantified by Rutherford backscattering spectroscopy. The distributions of the species within the films differ for the three tracer species. Molybdenum species, which migrate slower than Al^{3+} ions, are retained within the films, since they are unable to migrate to the pore base regions of the films. In contrast, hafnium and neodymium species, which respectively migrate at rates similar to and faster than Al^{3+} ions, are able to reach the pore base regions where they are lost to the electrolyte; the loss of the faster migrating-neodymium species is greater than that of hafnium species. The behaviours are related to the influence of flow of the alumina within the barrier layer on the transport of the tracer species.

Galvanostatic Growth of Nanoporous Anodic Films on Iron in Ammonium Fluoride-Ethylene Glycol Electrolytes with Different Water Contents

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

Journal of Physical Chemistry C, **114**, 18853-18859 (2010)

The growth of porous anodic films on iron has been examined at a constant current density of 50 A m^{-2} in 0.1 mol L^{-1} NH_4F-ethylene glycol electrolytes containing 0.1-1.5 mol L^{-1} water. Nanoporous films are formed in all the electrolytes, with the growth rate increasing with the decrease in the water content of the electrolyte. A barrier layer, in which a high electric field is applied during anodizing, thickens in proportion to the formation voltage at a ratio of 1.9 nm V^{-1}, regardless of the water content of the electrolyte. However. there is a transition water content between 0.3 and 0.5 mol L^{-1}. at which growth behavior changes. Above the transition level, the formation voltage is constant after an initial voltage rise, with the constant voltage slightly rising with a decrease in water content. In contrast, the formation voltage increases continuously to more than 150 V when the water contents are below the transition level. The anodic films are poorly crystalline and contain a significant amount of fluoride species. A high enrichment of fluoride species occurs near the metal/film interface when the water content in the electrolyte is below the transition level. Such enrichment is not as significant, or possibly absent, in electrolytes of increased water content.

Formation of Porous Anodic Titanium Oxide Films in Hot Phosphate/Glycerol Electrolyte

H. Habazaki, M. Teraoka, Y. Aoki, P. Skeldon and G.E. Thompson

Electrochimica Acta, **55**, 3939-3943 (2010)

The present study reveals the formation of porous anodic films on titanium at an increased growth rate in hot phosphate/glycerol electrolyte by reducing the water content. A porous titanium oxide film of 12 μm thickness, with a relatively low content of phosphorus species, is developed after anodizing at 5 V for 3.6 ks in 0.6 mol dm^{-3} K_2HPO_4 + 0.2 mol dm^{-3} K_3PO_4/glycerol electrolyte containing only 0.04% water at 433 K. The growth efficiency is reduced by increasing the formation voltage to 20 V, due to formation of crystalline oxide, which induces gas generation during anodizing. The film formed at 20 V consists of two layers, with an increased concentration of phosphorus species in the inner layer. The outer layer, comprising approximately 25% of the film thickness, is developed at low formation voltages, of less than 10 V, during the initial anodizing at a constant current density of 250 A m^{-2}. The pore diameter is not significantly dependent upon the formation voltage, being ~10 nm.

Amorphous-to-Crystalline Transition of Silicon-incorporated Anodic ZrO_2 and Improved Dielectric Properties

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

Electrochimica Acta, **55**, 3144-3151 (2010)

Sputter-deposited zirconium and Zr-16 at.% Si alloy have been anodized to various voltages at several formation voltages in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 298 K for 900 s. The resultant anodic films have been characterized using X-ray diffraction, transmission electron microscopy, Rutherford backscattering spectroscopy, glow discharge optical emission spectroscopy, and electrochemical impedance spectroscopy. The anodic oxide films formed on Zr-16 at.% Si are amorphous up to 30 V, but the outer part of the anodic oxide films crystallizes at higher formation voltages. This is in contrast to the case of sputter-deposited zirconium, on which the crystalline anodic oxide films, composed mainly of monoclinic ZrO_2, are developed even at low formation voltages. The outer crystalline layer on the Zr-16 at.% Si consists of a high-temperature stable tetragonal phase of ZrO_2. Due to immobile nature of silicon species, silicon-free outermost layer is formed by simultaneous migrations of Zr^{4+} ions outwards and O^{2-} ions inwards. An intermediate crystalline oxide layer, in which silicon content is lower in comparison with that in the innermost layer, is developed at the boundary of the crystalline layer and amorphous layer. Capacitances of the anodic zirconium oxide are highly enhanced by incorporation of silicon due to reduced film thickness, even though the permittivity of anodic oxide decreases with silicon incorporation.

Phase Transformation and Capacitance Enhancement of Anodic ZrO_2-SiO_2

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

Journal of the Electrochemical Society, **157**, C444-C451 (2010)

Capacitance enhancement of anodic oxide films on zirconium by adding silicon is reported here with correlation to the phase transformation of the oxide. The anodic oxide film formed on zirconium consists mainly of monoclinic ZrO_2, which changes to tetragonal ZrO_2 phase on the Zr-5.5 atom % Si. Further increase in the silicon contents to 10 and 16 atom % results in the formation of amorphous oxide up to 30 V, above which two-layered films, comprising an outer crystalline tetragonal-phase oxide layer and an inner amorphous layer, are developed. The relative thickness of the outer crystalline layer to the total film thickness increases with formation voltage. The highest capacitance of the anodic oxide films is obtained on the Zr-10 atom % Si. The changes in capacitance, permittivity and formation ratio of anodic oxide films with alloy composition are discussed with phase transformation and growth process of anodic oxides.

A Critical Assessment of the Mott-Schottky Analysis for the Characterisation of Passive Film-Electrolyte Junctions

F. La Mantia, H. Habazaki, M. Santamaria and F. Di Quarto

Russian Journal of Electrochemistry, **46**, 1306-1322 (2010)

The widespread use of the Mott-Schottky plots to characterize the energetics of passive film/electrolyte junction is critically reviewed in order to point out the limitation of such approach in describing the electronic properties of passive film as well in deriving the correct location of the characteristic energy levels of the junction. The frequency dependency of M-S plots frequently observed in the experimental data gathered in a sufficiently large range of frequency is extensively discussed for a relatively thick (160 nm) thermally aged amorphous niobia (alpha-Nb_2O_5) film immersed in electrolytic solution. The relatively simple equivalent electrical circuit describing an ideally blocking behaviour of the junction allows a direct comparison of the experimental data analysis based on the use of Mott-Schottky or amorphous semiconductor Schottky barrier interpretative models. Moreover the theoretical simulations of the M-S plots based on the theory of crystalline semiconductor suggest an electronic structure of the investigated passive film containing a distribution of localized electronic states deep lying in energy in agreement with the model of amorphous semiconductor Schottky barrier.

Physicochemical Characterization of Thermally Aged Anodic Films on Magnetron-Sputtered Niobium

F. La Mantia, M. Santamaria, F. Di Quarto and H. Habazaki

Journal of the Electrochemical Society, **157**, C258-C267 (2010)

The influence of thermal aging, at intermediate temperature (1 h at 250ºC) and in different environments, on the electronic and solid-state properties of stabilized 160 nm thick amorphous anodic niobia, grown on magnetron-sputtered niobium metal, has been studied. A detailed physicochemical characterization of the a-Nb_2O_5/0.5 M H_2SO_4 electrolyte junction has been carried out by means of photocurrent and electrochemical impedance spectroscopy as well as by differential admittance (DA) measurements. A change in the optical bandgap (3.45 eV) of niobia film has been observed after aging (3.30 eV) at 250ºC in air for 1 h. A cathodic shift (0.15-0.2 V) in the flatband potential of the junction has been observed. The frequency dependence of DA data agrees with expectations of the theory of amorphous semiconductor Schottky barrier. The fitting of both components of DA allowed to get information on the distribution of the electronic density of states as a function of energy and distance from the metal oxide interface. The DA measurements evidenced for vacuum-treated niobia film an insulating to semiconductor transition. These findings can help to explain the large changes in the measured values of capacitance, after aging, and the larger leakage current observed in niobia electrolytic capacitors.

Role of Cathodic Half-cycle on AC Etch Process of Aluminium

S. Ono and H. Habazaki

Corrosion Science, **52**, 2164-2171 (2010)

The AC etch process effectively expands the surface area of aluminium foil as compared with DC etch process. This study explored the effect of cathodic half-cycle. The cathodic half-cycle enhanced passivation of pits developed during the preceding anodic half-cycle, making pit nucleation random. Anodic pulse without cathodic half-cycle produced hollows, due to preferential pit nucleation on pits produced in the preceding anodic half-cycle. The open circuit before the cathodic half-cycle does not largely influence the etch factor, but etch film formation is largely suppressed. The precipitation of aluminium hydroxide may not have a crucial role in porous layer formation.

Influence of Phosphate Concentration on Plasma Electrolytic Oxidation of AZ80 Magnesium Alloy in Alkaline Aluminate Solution

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

Materials Transactions, **51**, 94-102 (2010)

Plasma electrolytic oxidation of AZ80 magnesium alloy in alkaline aluminate electrolytes develops $MgAl_2O_4$-based highly crystalline oxide coatings with the morphology changing largely with phosphate concentration in electrolyte. The thickness of the coatings increases with phosphate concentration from 5 μm in phosphate-free electrolyte to ~70 μm in the electrolyte containing 0.1 mol dm^{-3} phosphate after anodizing for 900 s. The formation of the latter thick coating is associated with intense sparking during, anodizing. The thick coatings formed in the electrolytes containing 0.075 and 0.1 mol dm^{-3} phosphate are highly cracked. In contrast, the coating formed in the electrolyte containing 0.05 mol.dm^{-3} phosphate is relatively uniform, showing the highest corrosion protection in 0.5 mol dm^{-3} NaCl solution. The coatings consist of two layers, comprising an outer thick layer with high concentration of aluminum and an inner thin magnesium-rich layer.

Anodic Oxides on InAlP Formed in Sodium Tungstate Electrolyte

A. Suleiman, P. Skeldon, G.E. Thompson, F. Echeverria, M.J. Graham, G.I. Sproule, S. Moisa, T. Quance and H. Habazaki

Corrosion Science, **52**, 595-601 (2010)

Amorphous anodic oxide films on InAlP have been grown at high efficiency in sodium tungstate electrolyte. The films are shown to comprise an outer layer containing indium species, an intermediate layer containing indium and aluminium species and an inner layer containing indium, aluminium and phosphorus species. The layering correlates with the influence on cation migration rates of the energies of In^{3+}-O, Al^{3+}-O and P^{5+}-O bonds, which increase in this order. The film surface becomes increasingly rough with increase of the anodizing voltage as pores develop in the film, which appear to be associated with generation of oxygen gas.

Incorporation and Migration of Phosphorus Species in Anodic Alumina Films Containing Tungsten Tracer Layers

F. Zhou, D.J. LeClere, S.J. Garcia-Vergara, T. Hashimoto, I.S. Molchan, H. Habazaki, P. Skeldon and G.E. Thompson

Journal of the Electrochemical Society, **157**, C437-C443 (2010)

Al-W nanolayers have been used previously to investigate the mechanism of formation of porous anodic films on aluminum in phosphoric acid. The present study considers the interactions of the tungsten tracer species and phosphorus species in the films and the consequence to the transport of the tracer. The findings showed that phosphorus species migrate inward and pass through the nanolayer of outwardly migrating tungsten species. Further, the migration behaviors indicated negligible influence of either species on the migration of the other.

Influence of Current Density on the Distribution of Tungsten Tracer in Porous Anodic Alumina Films

F. Zhou, D.J. LeClere, S.J. Garcia-Vergara, P. Skeldon, G.E. Thompson and H. Habazaki

Surface and Interface Analysis, **42**, 247-251 (2010)

Porous anodic alumina films have been much studied recently due to interest in the application of the self-ordered porosity in nanotechnological systems. Experimental investigations have identified anodising regimes that generate pores with a relatively high degree of long-range order. However, the growth mechanism of the films, and its relation to the ordering of pores, is only partially understood. In the present work, the growth processes are studied over a range of current densities for films formed in oxalic acid. The films are formed on sputtering-deposited substrates containing tungsten nanolayers that provide W^{6+} tracer species in the films. The distributions of tracer species are observed by scanning and transmission electron microscopes and the amounts of tracer species quantified by Rutherford backscattering spectroscopy. It is shown that the tungsten tracer remains within an inner region of the cells, with a tungsten-free region being present next to the pore walls during the growth of the anodic films. Further, the thickness of the anodic film relative to that of oxidised metal increases with increasing current density, which is associated with an increase in the efficiency of film formation. This behaviour is consistent with the formation of pores by flow of film material in the barrier layer to the pore wall regions.

Influence of Vacuum Annealing Conditions on the Surface Oxidation and Vacancy Condensation in the Surface of an FeAl Single Crystal

A. Yamauchi, M. Tsunekane, K. Kurokawa, S. Hanada and K. Yoshimi

Intermetallics, **18**, 412-416 (2010)

The influence of annealing atmosphere, temperature and time on the surface oxidation and vacancy condensation behavior of {111}-oriented single crystals of B2-type FeAl was investigated. AFM observation showed that as-annealed surfaces under a high vacuum were rugged and covered with a thin oxide film. The results obtained by TEM indicated that the thin oxide film was {001}-oriented κ-Al_2O_3 epitaxially grown on the {111}-oriented FeAl surface. AES measurements showed that the thickness of the oxide film was almost twice as thick as that of the passive

Al_2O_3 film formed on the FeAl surface in an ambient atmosphere. It was found that the growth of surface mesopores is attributable to both the condensation of supersaturated vacancies in FeAl substrate and the Kirkendall effect by the surface oxidation during the vacuum annealing.

Oxidation Behavior of β-SiAlONs Prepared by a Combination of Combustion Synthesis (CS) and Spark Plasma Sintering (SPS).

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

Corrosion Science, **52**, 1738-1745 (2010)

The oxidation of β-$Si_{6-z}Al_zO_zN_{8-z}$s (z = 1, 2, and 3) prepared by a combination of combustion synthesis (CS) and spark plasma sintering (SPS) was investigated. The oxidation experiments were conducted at temperatures of 1000, 1200, and 1400ºC in air for 100 h (360 ks). Their oxidation kinetics follows a parabolic rate law, and the deviation from that increases with a decrease in the z value. The results of XRD and EPMA show that the oxide formed on β-SiAlONs (z = 1 and 2) consists of silica and mullite, and on β-SiAlON (z = 3) of only mullite.

Microstructure and Analysis of Oxide Scales Formed on Cr-Si-Ni Compacts in Air and H_2O-containing Atmospheres.

A. Yamauchi, Y. Suzuki, N. Sakaguchi, S. Watanabe, S. Taniguchi and K. Kurokawa

Corrosion Science, **52**, 2098-2103 (2010)

The purpose of this study was to characterize the oxide scales formed on various Cr–Si–Ni compacts at 1273 K in air and H_2O-containing atmosphere by TEM. It was found that $CrSi_2$–(5–20)mass%Ni compacts form double layer scales, consisting of an outer Cr_2O_3 layer and an inner SiO_2 layer. The oxide scale changed from SiO_2- to Cr_2O_3-based scale with an increase in the Ni concentration. However, it was observed that the oxide scale formed in H_2O-containing atmospheres showed local SiO_2 growth into the substrate. This result suggests that the inward oxidant diffusion promotes the local growth of SiO_2 in the H_2O-containing atmospheres.

Spark Plasma Sintering of binderless n-WC and n-WC- X (X=Nb, Re, Ta, Ti, B, Si)

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

Transactions of JWRI, **39**, 47-56 (2010)

Nano sized tungsten carbide (n-WC) compacts with and without grain growth inhibitors were synthesized by Spark Plasma Sintering (SPS) with different heating rates. The microstructure and mechanical properties of the various samples were compared. Grain growth inhibition effects increased in the order Nb>Re>Ta>Ti and with increasing heating rate. Addition of Si and B increases grain growth, but suppresses the formation of the brittle semi carbide (W_2C) phase. Using the WC-X phase diagram and the sintering rate curves, we try to generalize the effect of various grain growth inhibitors on the sintering of n-WC.

Effects of Additional Elements and Cooling Rates on Microstructures of Sn-Ag-Cu Solders

S. Kirai, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka

16th Symposium on “Microjoining and Assembly Technology in Electronics”, **16**,
141-146 (2010)

In order to clarify the influences of composition and cooling rates on the microstructures of Sn-Ag-Cu solders, some Sn-Ag-Cu alloys were solidified at different cooling rates. 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 or In resulted in further refinement of primary and Sn-Ag_3Sn eutectic phases. (in Japanese)

Analysis of Reaction Behavior of Fe-based Alloys with Additional Elements in Molten Lead-free Solders

T. Kamamoto, A. Yamauchi, S. Kawakubo, A. Irisawa, K. Kurokawa and J. Tanaka

16th Symposium on “Microjoining and Assembly Technology in Electronics”, **16**,
229-234 (2010)

The solder baths used in the wave soldering are made from various kinds of steel. Reaction behavior of Fe-based alloys in molten Sn-3.0%Ag-0.5%Cu solders was investigated in the present study. A $FeSn_2$ layer is formed in all the specimens in the interfacial reaction at 623 to 723 K. Carbon steel with Cr or Ti shows a smaller thickness loss due to suppression of interfacial reaction than carbon steel without Cr and Ti. On the other hand, the addition of Mo to carbon steel does not improve the resistance against interfacial reaction because of the formation of Mo rich ferrite phase which is corroded easily. These results indicate that the microstructure of metal substrate has influence on the interfacial reaction. The thickness loss of carbon steel with Cr follows a parabolic law. (in Japanese)

Relation between Microstructure and Hardness of Sn-Low Bi Alloys

T. Yokota, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka

20th Symposium of Micro Electronics, **20**, 55-58 (2010)

The purpose of the study is to clarify change in microstructure and hardness of Sn-low Bi alloys with Bi content. The microstructure observation and DSC measurement demonstrated that a Bi-rich phase is formed at grain boundaries or in Sn grains, in Sn-Bi alloys with Bi content more than 3 mass%, and the eutectic crystallized in the alloys with Bi content more than 6.75 mass% . The measurement of hardness for the primary β-Sn phase indicated that the hardness was almost identical in all alloys with Bi content than 5 mass%. After aging at 150℃, fine Bi particles precipitated throughout the whole of the matrix due to the interdiffusion between β-Sn and Bi rich phase. (in Japanese)

Effect of Ni Addition on Structure of Sn-Ag-Cu/Cu Solder Joint

A. Yamauchi and J. Tanaka

20th Symposium of Micro Electronics, **20**, 71-74 (2010)

Microstructures and morphologies of interfacial reaction layers between Cu and Sn-Ag-Cu with and without Ni have been investigated to reveal the effect of Ni concentration on the interfacial reaction layer. Sn-3.0Ag-0.5Cu-xNi solders (x=0, 0.05, 0.1, 0.2, 0.5 mass%) were prepared. Sn-Ag-Cu solder formed Cu-Sn intermetallic compound as irregularly reaction layer at the interface between Cu and solder. On the other hand, uniform reaction layers that consist of granular Cu-Ni-Sn compound formed at the interface between Cu and Sn-Ag-Cu-Ni solders. The thickness of the reaction layer between Cu and solder with Ni was the minimum in SAC-0.05%Ni. (in Japanese)

Analysis of High Temperature Corrosion and Wear Damage on Furnace Water Wall in Pulverized Coal Firing Boiler

S. Kyo, M. Nakamori, K. Kurokawa and T. Narita

Zairyo-to-Kankyo, **59**, 456-463(2010)

Recently, a pulverized coal firing boiler is getting large capability; therefore, it should take a further effective environmental measure. As a facility aspect, it takes a measure to inhibit the amount of generation of NO_x and, in operation aspect; it is operated by low O_2 combustion. As a result, in the combustion chamber, it becomes low O_2 atmosphere because of lack of oxygen and also the sulfide corrosion becomes actualized because of H_2S. In addition to that, it is recognized that it accelerates damages by multiple influences from erosion damage by steam blast from the wall blower to remove slag. The damage behavior around wall blower in the investigated boiler is as follows. ①Steam erosion by direct collision of high temperature and high pressure steam. ②The coal ash that was caught in the current of steam injection and collided on the tube surface causes the ash erosion. ③The steam that is lower temperature than the tube temperature collides onto the tube surface which is exposed by high temperature combustion gas and that causes the thermal collision. The synergistic result of those 3 physical collisions causes a crack and delamination in the scale. Moreover, because of the above results, when the nascet metal aspect is exposed it is directly contacted with combustion gas. And that prompts the high temperature corrosion response and it is accumulated. For that result, it was concluded that the damage has been accelerated. (in Japanese)

The Sintering Kinetics of n-WC-Si and n-WC-B

K. Nanda Kumar, M. Watanabe and K. Kurokawa

Applied Plasma Science, **18**, 83-86(2010)

Nano scale (~70 nm) WC (n-WC) powders with minimal amounts of either Si or B additions ere compacted by Spark Plasma Sintering (SPS). The sintered compacts were seen to exhibit strikingly different microstructures: excessive abnormal grain growth in the WC-Si sample and large isotropic grain growth in the WC-B compacts. To clarify the mechanisms behind the microstructural evolution, sintering was interrupted at various temperatures and the kinetics of grain growth was analyzed. The observations suggest that there is a preferential wetting of the WC grains by the liquid phase responsible for the coarsening process. The observed relation between the grain size and stroke change rate is explained on the basic of the rate equations for densification and coarsening.

Application of Flake Shaped Glass (Glass Flake) Filler for Dental Composite Resin

Motohiro Uo, Akiko Sasaki, Junko Masuda, Juichi Ino and Fumio Watari

Journal of Ceramic Society of Japan, **118**(6), 425-427 (2010)

For dental composite resin (CR), mechanical strength, estheticity and flowability are required. In this study, flake-shaped glass (FSG; Glass Flakeμ) was employed as the filler of CR. FSG is composed of thin glass platelets with a flat, smooth surface. FSGfilled CR (FSG/CR) showed good transparency compared to an irregularly shaped filler. The Vickers hardness of FSG/CR was increased with increasing FSG content and was comparable to that of a commercial CR at 70 wt %FSG content. The compressive strength of FSG/CR with silanized FSG was also comparable to that of the commercial CR. The flowability of uncured FSG/CR was much higher than that of the CR containing the irregularly shaped filler and that of commercial flowable CR with the same filler content. Thus, FSG will be useful as a filler of dental CR that provides estheticity, mechanical strength and flowability.

A Study of Zinc Contained in Yellow and Black Discolored Nails by X-ray Fluorescence and X-ray Absorption Fine Structure Analyses

Motohiro Uo, Kiyotaka Asakura, Erika Watanabe, Inkin Hayashi, Teruki Yanagi,
Hiroshi Shimizu and Fumio Watari

Nano Biomedicine, 2, 103-106 (2010)

The elements in discolored nails were assessed by X-ray fluorescence analysis (XRF), and the chemical state of Zn in the nail samples was assessed by X-ray absorption fine structure (XAFS) analysis. Compared to the normal nail, a part of the yellow nail contained a considerably high amount of Ca, whereas the black nail contained higher amounts of Ca and Zn. The chemical state of Zn in the yellow nail was similar to that in the normal nail. The Zn in the black nail was in a slightly different chemical state, suggesting the existence of different chemical species of Zn in the black nail.

Thin Films of Single-Walled Carbon Nanotubes Promote Human Osteoblastic Cells (Saos-2) Proliferation in Low Serum Concentrations

Tsukasa Akasaka, Atsuro Yokoyama, Makoto Matsuoka, Takeshi Hashimoto
and Fumio Watari

Materials Science and Engineering C, 30, 391-399 (2010)

One strategy used for the regeneration of bone is the development of cell culture substrates and scaffolds that can control osteoblast proliferation and differentiation. In recent investigations, carbon nanotubes (CNTs) have been utilized as scaffolds for osteoblastic cell cultures; however, there are only a few reports describing the

proliferation of osteoblastic cells on thin CNT films; in particular, the effects of serum concentration on cell proliferation have not been studied. In the present study, we prepared culture dishes with homogeneous thin or thick films of non-modified CNTs and examined the effect of serum concentrations on human osteoblastic cells (Saos-2) proliferation in these culture dishes. We demonstrated that the ratio of cell proliferation was strongly affected by the concentration of serum. Interestingly, singlewalled carbon nanotube (SWNT) thin films were found to be the most effective substrate for the proliferation of Saos-2 cells in low concentrations of serum. Thus, thin SWNT films may be used as an effective biomaterial for the culture of Saos-2 cells in low serum concentrations.

The Bactericidal Effect of Carbon Nanotube/Agar Composites Irradiated with Near-Infrared Light on *Streptococcus Mutans*

Tsukasa Akasaka, Makoto Matsuoka, Takeshi Hashimoto, Shigeaki Abe, Motohiro Uo and Fumio Watari

Materials Science and Engineering B, 173, 187-190 (2010)

Dental caries are mainly associated with oral pathogens, and Streptococcus mutans is a primary cariogenic organism. Many methods have been established to eliminate S. mutans from the oral cavity. This study aimed to evaluate the effect of carbon nanotube (CNT)/agar composites irradiated with near-infrared (NIR) light on S. mutans, as a potential photothermal antimicrobial nanotherapy. A colony-forming unit assay clearly showed that CNT/agar composites attain bactericidal activity after NIR light irradiation; this bactericidal activity is higher than that of graphite (GP)/agar and activated carbon (AC)/agar composites. Furthermore, it was observed that longer irradiation times immobilized S. mutans in the CNT/agar composite.

Microstructure Evaluation of the Interface between Dental Zirconia Ceramics and Veneering Porcelain

Yohei Kawai, Motohiro Uo and Fumio Watari

Nano Biomedicine, **2**(1), 31-36 (2010)

The application of zirconia ceramics for the dental restorations and dental implants has increased. However the weak performance of the veneering porcelains and low adhesion to the zirconia framework were reported. In this study, the microstructure, elemental distribution and crystal phase around the interface between zirconia and veneering porcelain were estimated using SEM-EDS (energy dispersed spectrometry) and micro-XRD (X-ray diffraction). The specimen fired at 940°C for 1 minute showed clear interface in the SEM and the elemental distribution images of Zr and Si. With extending firing period up to 384 hours, slight diffusions of Zr and Si, which are the major components of zirconia and porcelain ware suggested. In micro-XRD, no phase transformation was observed in the zirconia and porcelain, thus extension of firing period would not affect the crystal phase around the zirconia/porcelain interface. Therefore, the extension of firing period was expected to slightly improve the zirconia/porcelain bonding.

Culture of ES Cells and Mesenchymal Stem Cells on Carbon Nanotube Scaffolds

Hiromi Kitahara, Yoshinori Kuboki, Hiroko Takita, Tsukasa Akasaka, Fumio Watari and Nobuo Inoue

Nano Biomedicine, **2**(2), 81-92 (2010)

Cell proliferations on carbon nanotube scaffolds were investigated for the embryonic stem cells (ES cells) of mouse and the bone marrow-derived mesenchymal stem cells (MSC) of rat. Although ES cells were well attached and proliferated on gelatin-coated plastic dishes, they did not attach on the CNT-coated scaffold, and formed the spheroids growing in the culture medium. For MSC, they attached on the CNT-coated scaffold and grew to form mineralized particles as on the plastic dishes of control. The growth rate of the MSC was lower than control but showed the higher expression of alkaline phosphatase activity per cell in 2 weeks and degree of mineralization per cell for 3 and 4 weeks.

Highly Sensitive Detection and Quantitative Analysis of Ultra Low Concentration of Carbon Nanotubes by Absorptiometric Method

Sachiko Itoh, Yasutaka Yawaka and Fumio Watari

Nano Biomedicine, **2**(2), 130-138 (2010)

It is important to know quantitatively the dilute concentration of carbon nanotubes (CNTs) for the view point of their risk assessment and biomedical applications. However, the measurement of less than 100 ppm is difficult for the conventional weight measuring method. In this study, the optical absorptiometric method was newly proposed and its validity was investigated. The method showed the linear relationships between absorption and CNT concentrations in the range from 3 ppm to 100 ppm for various solutions, with or without proteins and phenol-red in the medium at different pH, and for various wave lengths. The higher sensitivity than the conventional weight measuring method and the validity in the various conditions suggested that the newly developed absorptiometric measuring method is efficient for the quantitative analysis of CNTs in the low concentration range.

Strong Adhesion of Saos-2 Cells to Multi-walled Carbon Nanotubes

Makoto Matsuoka, Tsukasa Akasaka, Yasunori Totsuka and Fumio Watari

Materials Science and Engineering B*,* **173**(1-3), 182-186 (2010)

In recent years, carbon nanotubes (CNTs) have been considered potential biomedical materials because of their unique character. The aim of this study was to investigate the response of a human osteoblast-like cell line – Saos-2 – on single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). The surface of a culture dish was coated with CNTs, and Saos-2 cells were cultured for three days. Cell morphology, viability, alkaline phosphatase (ALP) activity, adhesion, and vinculin expression were evaluated. The result showed high cell viability and strong adhesion to MWCNTs. Saos-2 cultured on MWCNTs exhibited vinculin expression throughout the cell body, while the cells attached to SWCNTs and glass were mostly limited to their periphery. Our results suggest that CNT coatings promote cell activity and adhesiveness. These findings indicate that MWCNTs could be used as surface coating materials to promote cell adhesion.

Transmission Electron Microscopic Observation of Cells Cultured on Multiwalled Carbon Nanotube-Coated Sponges

E. Hirata, N. Sakaguchi, M. Uo, N. Ushijima, Y. Nodasaka, F. Watari, H. Ichinose and A. Yokoyama

Journal of Electron Microscopy, 59, 447-50 (2010)

The cell structure and interface between cultured cells and a multiwalled carbon nanotube (MWCNT)-coated sponge (MWCNT-coated sponge) were observed by transmission electron microscopy (TEM). Moreover, the atomic structure of

MWCNTs that entered the cells was also examined by means of high-resolution TEM (HRTEM). MWCNTs were observed in the cytoplasm, and a few MWCNTs were recognized in the cell nuclei. Those MWCNTs maintained their structure there. Subcellular organelles did not appear to be different from those on the collagen sponge despite the cellular uptake of MWCNTs.

Interaction of Water Molecules with Graphene: A DFT and MD Study

Shigeaki Abe, Yoshiaki Nagoya, Fumio Watari and Hiroto Tachikawa

Jpn. J. Appl.Phys., 49, p01AH071-01AH074 (2010)

Water evaporation processes from the edge region of graphene sheet have been investigated by means of direct molecular dynamics-molecular orbital (MO-MD) method. Five graphenes with n=1, 7, 19, 37 and 61 (where n is numbers of benzene rings in graphenes) were examined as models of graphene sheets. The edge carbons of each graphene were terminated by hydrogen atoms. The oxygen atom of water molecule binds to one or two C-H hydrogen atoms of the edge carbons in H_2O-graphene interaction system. The binding energy of H_2O increased gradually as a function of n and was saturated around n=61. At low temperature (10-100 K), the water molecule was still connected to the graphene sheet, whereas the evaporation of H_2O was found above 300 K. The mechanism of water evaporation was discussed on the basis of theoretical results.

Internal Distribution of Micro-/Nano-Sized Ceramics and Metals Particles in Mice

Shigeaki Abe, Ikuhiro Kida, Mitsue Esaki, Nobuki Iwadera, Mami Mutoh, Chika

Koyama, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki, Manabu Morita,
Yoshinori Sato, Koichi Haneda, Tetsu Yonezawa, Balachandran Jeyadevan,
Kazuyuki Tohji, and Fumio Watari

J. Ceramic Society of Japan, 118, p525-529 (2010)

Internal distribution of several nanoparticles in mice has been investigated using scanning X-ray analytical microscopy, magnetic resonance imaging and inductively coupled plasmaatomic emission spectroscopy. According dynamic laser scattering analysis, the actual particle size of obtained metal oxide was similar to that of metal particles. The estimated diameters were ca. one micrometer. After administration through the tail vein of the mice, metal particles quickly reached some organs. The distribution ratio reached a constant value and was then maintained. On the other hand, the metal oxide particles were first localized in the spleen and lung. The concentration in the lung was decreased with post-injection time. This result suggested that the particles were temporally trapped in the lung then removed to other organs. The behaviors between metal and metal oxide were quite different even when those particles had a similar actual particle size. Therefore, the distribution behavior of particles depended on the chemical species.

Direct ab-initio MD Study on the Interaction of Hydroperoxy Radical (HOO) with Water Molecules

Hiroto Tachikawa, and Shigeaki Abe

Phys. Chem. Chem. Phys., 12, p3904-3909 (2010)

Structures and electronic states of the HOO radical interacting with water molecules, expressed by $HOO(H_2O)_n$ (n = 1 and 2), have been investigated by means of a direct *ab initio* molecular dynamics (MD) method. From the static *ab initio* calculation of $HOO–H_2O$ complex, two types of HOO radical were found: *i.e.*, the HOO radical acts as a hydrogen donor or acceptor in the complex (n = 1). The binding energies of former and latter complexes were calculated to be 8.7 and

3.3 kcal mol^{-1}, respectively, at the QCISD/6-311++G(2d,2p) level. In the case of 1 : 2 complex $HOO(H_2O)_2$, a cyclic structure with a hydrogen donor of HOO was obtained as the stable form. Effects of zero point vibration on the structures and hyperfine coupling constants of the HOO radical were also investigated. The structures and electronic states of $HOO(H_2O)_n$ (n = 1 and 2) were discussed on the basis of theoretical results.

Photophysical Characterization of Cumarin Doped Poly (Lactic Acid) Micro Particles and its Fabrication for Bioimaging

Shigeaki Abe, Takayuki Kiba, Kiyotada Hosokawa, Satoru Nitobe, Takashi Hirota, Hirohisa Kobayashi, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki, Shin-Ichiro Sato, Fumio Watari, Iosif D. Rosca

J. Electron Spectroscopy and Related Phenomena, 181, p181-185 (2010)

We prepared fluorescent coumarin dye-doped poly (acrylic acid) microparticles, which are well known as a biodegradable polyester, and the photophysical properties were characterized by scanning electron microscope, atomic force microscope and spectroscopic investigation. Spherical particles with diameters ranging from 0.5 to a few μm were obtained. Based on spectroscopic investigation, the internal environment was close to that of a polar solvent such as methanol, and the dyes were dispersed without aggregation inside the particles. The obtained particles were administered to a mouse through the tail vein, and the biodistribution was then observed after some organs were excited at 1 day and 1 week post-injection. The particles were accumulated in the organs, especially in the lung and spleen. After injection, the particles were trapped temporally in the lung, then seemed to be transported to other organs by blood circulation. This tendency is similar to the biodistribution of TiO_2 microparticles that we have reported previously.

Structure and Eletronic States of Water Molecules on Nanocarbon Materials: A DFT and MD Study

Shigeaki Abe, Yoshinori Nagoya, Fumio Watari and Hiroto Tachikawa

Jpn. J. Appl. Phys., 49, p06GJ131-06GJ133 (2010)

Effects of water molecules on the electronic states of graphene have been investigated by means of density functional theory (DFT) and timedependent DFT methods at the PW91PW91 and B3LYP/6-31G(d) levels of theory. Solvation caused by one to four water molecules (n=1-4) was examined in the present study. A graphene composed of 14 benzene rings was used as a model of finite-sized graphene ($C_{42}H_{16}$). The water molecules interact with the graphene surface via hydrogen bonding. The band gap of graphene was slightly red-shifted by the solvation. This shift was caused by the formation of hydrogen bonds between H_2O and the graphene surface. The electronic states of the graphene–water system were discussed on the basis of theoretical results.

Morphology-controlled Calcification ($CaCO_3$): A Donut-shape Crystal Growth Breaking Through a Carbon Nanotube "Blanket"

Shigeaki Abe, Tomoki Ishida, Chika Koyama, Tsukasa Akasaka, Motohiro Uo, and Fumio Watari

J. Australian Ceramic Society 46 (2), p48-53 (2010)

Biomimetic calcification has been investigated using poly-carboxylated compounds as calcium ion (Ca^{2+}) collectors. In this study, a poly-carboxylated carbon nanotube was synthesized as an ion collector. Using the carbon nanotube derivative for calcification, the morphology and polymorph of $CaCO_3$ were controlled. Nanosized calcium carbonate was selectively produced depending upon the reaction time by using the carbon nanotube derivatives. The crystal grew in a carbon nanotube

"knitted blanket"; then the product broke through the blanket by further growth of the crystal and reached the surface. In addition, a unique doughnut-like morphology of calcite, a major polymorph of $CaCO_3$, proceeded from the 24-hour reaction.

Suitable Condition for Sidewall Carboxylation of Multi-Walled Carbon Nanotube

Tomoya Takada, Desharin Santida and Shigeaki Abe

Nano Biomedicine 2(2). P147-152 (2010)

Reaction conditions for sidewall carboxylation of multi-walled carbon nanotubes (MWCNTs) by radical addition reaction using acid peroxide as the radical source were investigated with the goal of high-yield carboxylation. In particular, the parameters of reaction time and reactant (succinic acid peroxide) concentration were examined. The carboxylation ratio is defined as the ratio of the mole of carboxylic group to the molar amount of carbon in the MWCNT. It was concluded that the carboxylation ratio depends more on reactant concentration rather than on reaction time. This ten-dency is reasonably explained by assuming that the carboxylation will be almost complete within a short period, and the yield of carboxylation will ultimately reach a constant value. The final value of the carboxylation ratio is hence determined by the reactant concentration. The results were explained by the kinetics of pseudo-first-order reaction.

Refinement of Oxide Particles by Addition of Hf in Ni-0.5 mass %Al-1 mass%Y_2O_3 Alloys

Q. Tang, T. Hoshino, S. Ukai, B. Leng, S. Hayashi and Y. Wang

Materials Transaction **51(11),** 2019-2024 (2010)

The effect of adding minor elements, such as Ti, Mg, Zr, Ca or Hf, on the size of oxide particles was investigated in Ni-based ODS alloy, Ni-0.5 mass%Al-1 mass %Y_2O_3. Among these elements, Hf is the most effective at refining the oxide particles, particularly at a concentration of 0.8 mass% Hf, as verified by TEM observation and hardness measurement. X-ray diffraction measurements indicate that the formation of $Y_2Hf_2O_7$ is responsible for the refinement of oxide particles. The Hf is also effective for a commercial superalloy of PM1000.

Formation of Residual Ferrite in 9Cr-ODS Ferritic Steels

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

Materials Science and Engineering A **527,** 4418–4423 (2010)

It is recognized that the high-temperature strength of 9Cr-ODS ferritic steels is maintained by the presence of a ferrite phase. In order to clarify the formation process of the ferrite phase, 9Cr-ODS ferritic steels containing various contents of Y_2O_3, i.e., 0 mass%, 0.1 mass%, 0.35 mass%, and 0.7 mass%, are prepared by means of mechanical alloying and hot-pressing. The ferrite phase is formed by the addition of 0.35 mass% and 0.7 mass% Y_2O_3; however, it is not formed for steels without and with 0.1 mass% Y_2O_3 normalized for 1 h at 1050 ◦C. It is considered from the thermodynamic analyses that the pinning of the $\alpha-\gamma$ interface motion by the dispersed Y–Ti complex oxide particles can be attributed to the retention of the ferrite phase normalized at 1050 ◦C, and this ferrite phase cannot be δ-ferrite that is in equilibrium with the γ-phase.

Microstructural Characterization of Nb-Al Base ODS Alloys

S. Ukai, A. Minami, S. Hayashi, N. Sakaguchi and S. Miura

Materials Science Forum Vols. **654-656**, 436-439, (2010)

Nb, Al and Y_2O_3 powders were mechanically alloyed together with 5 wt% stearic acid. The heavy plastic deformation of the powders by mechanical alloying led significant hardening to 970 Hv and the reduced grain size to 10 nm. Nb-Al base ODS alloys consolidated by HIP at 1500 ºC and 150 MPa for 0.5 h gave the dual phase of Nb solid solution and Nb_3Al compound. The oxide particles are of the hexagonal type $YAlO_3$ (YAH), with the size of 50 nm to 200 nm. The high-temperature ductility at 1200 ºC and capability of the grain growth at 2000 ºC were confirmed.

Microstructure and Tensile Properties of ODS Ferritic Steels Produced by Mechanical Alloying in Argon and Hydrogen Gas Environments

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

Materials Science Forum Vols. **654-656**,166-169, (2010)

Two types of oxide dispersion strengthened (ODS) ferritic steels have been produced by mechanical alloying (MA) either in argon or in hydrogen atmosphere, and vacuum hot pressing (VHP). A drastic reduction in the oxygen and nitrogen contents after VHP was strongly affected by hydrogen gas used as the MA atmosphere. MA in hydrogen was found to be effective for refining the steel matrix and enhancing the tensile ductility of the ODS ferritic steels.

Effects of Zr Addition on the Microstructure of 14%Cr-4%Al ODS Ferritic Steels

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

Materials Transaction **51(5),** 1011-1015 (2010)

DS ferritic steels have a good radiation resistance, high creep strength and a good swelling resistance. In such alloys, Zr is used to improve the creep properties by stabilizing the grain boundaries. The influence of the zirconium on the microstructure will be discussed is this study. The addition of Zr reduces strongly the number density of the inclusion distribution. The reduction factor is between 4 (transverse direction) to 15 (longitudinal direction). The addition of Zr reduces the formation of Al and Y oxide (micro scale). The carbide composition is also different according to the material composition. Zr-free material forms W/Ti carbides and Zr-added material forms Zr/Ti carbides without formation of W carbides (free enthalpy). Zr addition may be considered as very good in terms of strength and corrosion resistance.

High-Temperature Mechanical Properties and Microstructure of 9Cr Oxide Dispersion Strengthened Steel Compared with RAFMs

Y. Li, T. Nagasaka, T. Muroga, A. Kimura, S. Ukai

4th Int. Conf. on Sperstrong Field in Plasmas, (2010)

In this work, high-temperature mechanical properties and microstructure of a 9Cr-ODS steel were studied. The properties were compared with those of normal reduced activation ferritic/martensitic steels (RAFMs) of CLAM and JLF-1. The tensile strength of the 9Cr-ODS steel was almost twice the values of

the RAFMs at all test temperatures, and the strength level at 923 to 973 K was comparable to those of the RAFMs at 823 K. The 9Cr-ODS steel also exhibited a superior creep strength. Prediction with Larson-Miller parameter for the typical blanket conditions suggested that the 9Cr-ODS steel can successfully extend the maximum operation temperature to ~923 – 973 K. The 9Cr-ODS steel has a tempered martensitic structure with uniform oxide particles in the matrix. After creep tests, the mean diameter and density of the oxide particles were not changed significantly by different creep temperatures and stresses, suggesting the stability of the microstructure.

Rapid Formation of α-Al_2O_3 Scale on an Fe–Al Alloy by Pure-Metal Coatings at 900°C

Y. Kitajima, S. Hayashi, T. Nishimoto, T. Narita, and S. Ukai

Oxidation of Metals, 73, 375–388, (2010)

Rapid formation of an α-Al_2O_3 scale on Fe–50 at.%Al by pure metal thin coatings of Ni, Al, Ti, Cr or Fe was investigated, and the effects of those elements on Al_2O_3-scale evolution were assessed. The oxidation behavior of samples with and without coatings could be divided into two groups: the samples with/without Ni and Al, and those with Ti, Cr and Fe. The mass gains of samples coated with Al and Ni were almost the same as that of non-coated Fe–50 at.%Al alloy. The mass gains of samples coated with Ti, Cr, and Fe were much lower than that of the Fe–50 at.%Al alloy. A stable α-Al_2O_3 scale was found to develop from the beginning of oxidation on the samples coated with Ti, Cr and Fe. However metastable θ-Al_2O_3 remained after long-time oxidation of non-coated and Ni- and Al-coated samples. The direct α-Al_2O_3 scale formation on the samples with Cr or Fe coatings was speculated to be due to sympathetic nucleation of α-Al_2O_3 on the surface of Al-supersaturated Fe_2O_3 for Fe-coated sample, and composition changes from $(Cr,Al)_2O_3$ to $(Al,Cr)_2O_3$ for the Cr-coated sample. Initial formation of an oxide having a

corundum structure was inferred to provide a nucleation site for precipitation of α-Al_2O_3 without prior formation of a metastable Al_2O_3 scale.

Oxidation Behavior of Ni-3, 6 wt% Al Alloys at 800°C in Atmospheres Containing Water Vapor

S. Hayashi, S. Narita, T. Narita

Oxidation of Metals, 74, 33–47, (2010)

The oxidation behavior of Ni, Ni–3Al, and Ni–6Al alloys at 800°C in air+H_2O was investigated. The oxidation kinetics of Ni and the alloys in air+H_2O were very similar, but the mass gains of Ni and each alloy were smaller in air+H_2O than in air. Oxidation products formed on Ni-3 and 6Al alloys consisted of an outer NiO scale and internal Al_2O_3 precipitates. The growth rates of both NiO and the internal oxidation zone were much smaller in air+H_2O. The NiO scale formed in air+H_2O was duplex in structure with outer porous and inner dense layers. The outer porous layer consisted of fine powder-like NiO particles. A thicker metallic Ni(Al) layer formed at the NiO/alloy interface in air+H_2O, caused by extrusion of Ni from the substrate due to volume changes accompanying the internal oxide formation. Formation of the metallic Ni layer appeared to be the reason for the similarity between the oxidation kinetics of both Ni and the alloys in air+H_2O.

Studies on Heterogeneous Degradation of Polypropylene/Talc Composite: Effect of Iron Impurity on the Degradation Behavior

Hisayuki Nakatani, Hiroshi Shibata, Kensuke Miyazaki, Tetsu Yonezawa,
Hidetoshi Takeda, Yutaka Azuma, and Shin Watanabe

Journal of Applied Polymer Science, **115(1)**, 167-173 (2010).

In this study, an effect of iron oxide (Fe_2O_3) impurity in talc on degradation behavior of polypropylene (PP)/talc composite was studied using a PP/ Fe_2O_3 model composite sample. The thermal oxidative degradation was performed at 100 degrees C. Although the degradation of a pure PP sample hardly occurred at such temperature, the existence of Fe_2O_3 inciuced the PP degradation. The degraded PP part was formed around the Fe_2O_3 grain in the PP/ Fe_2O_3 sample. It was found from the optical microscope observation that the degraded PP was able to diffuse only within the PP amorphous part. The analysis of the oxidation distribution on the degraded PP surface was performed employing a scanning electron microscope/ electron dispersive spectrometer. The result showed that the PP spots in the vicinity of the Fe_2O_3 grain were unoxidized during the initial degradation process, and the oxidized PP spots were located at around 6 mu m distance from the Fe_2O_3 grain. It was concluded that the degradation was initiated microscopically away from the Fe_2O_3 grain so that the Fe_2O_3 had both the abilities to accelerate the decomposition of PP hydroperoxide compounds and to reduce the produced radical species into nonradical products.

Corrosion of Al-Sn-Bi Alloys in Alcohol at High Temperatures. Part I: Effects of the Metallurgical Structure of the Alloys and the Metal Salt Additions to Alcohol

Tatsuya Kikuchi, Yasuhito Hara, Masatoshi Sakairi, Tetsu Yonezawa, Akira Yamauchi, and Hideaki Takahashi

Corrosion Science, **52(4)**, 1482-1491 (2010).

Corrosion of free machining Al alloys that contain Sn and Bi was investigated at 391-415 K in 2-(2-(2-methoxyethoxy)ethoxy)ethanol (MEEE) and 2-(2-(2-butoxyethoxy)ethoxy)ethanol (BEEE) with/without $SnCl_2$, $Sn(OC_2H_5)(4)$, FeCl3, and $CuCl_2$. The Al-Sn-Bi alloy displayed severe pitting corrosion in MEEE similar to the Al-Sn alloy in BEEE at 415 K, and Sn and Sn/Bi were enriched on the surface of pits. Immersion tests of pure Al in MEEE containing Sn/Cu-salts at 415 K also showed severe corrosion and the deposition of metallic Sn and Cu on the surface. The corrosion mechanisms are discussed in terms of the electro-catalytic activity of the Sn enriched on the surface.

Self-Assembly Method of Linearly Aligning ZnO Quantum Dots for a Nanophotonic Signal Transmission Device

T. Yatsui, Y. Ryu, T. Morishima, W. Nomura, T. Kawazoe, T. Yonezawa, M. Washizu, H. Fujita, and M. Ohtsu

Applied Physics Leters, **96(13)**¸133106 (2010).

We report a self-assembly method that aligns nanometer-sized quantum dots (QDs) into a straight line along which photonic signals can be transmitted by optically near-field effects. ZnO QDs were bound electrostatically to DNA to form a one-dimensional QD chain. The photoluminescence intensity under parallel polarization excitation along the QDs chain was much greater than under perpendicular polarization excitation, indicating an efficient signal transmission along the QD chain. As optical near-field energy can transmit through the resonant energy level, nanophotonic signal transmission devices have a number of potential applications, such as wavelength division multiplexing using QDs of different sizes.

Corrosion of Al-Sn-Bi Alloys in Alcohols at High Temperatures. Part II: Effect of Anodizing on Corrosion

Tatsuya Kikuchi, Yasuhito Hara, Masatoshi Sakairi, Tetsu Yonezawa, Akira

Yamauchi, and Hideaki Takahashi

Corrosion Science, **52(8)**, 2525-2534 (2010).

Nine kinds of Al alloys were anodized to form porous anodic oxide films, and then anodized specimens were immersed in 2-(2-(2-methoxyethoxy)ethoxy)ethanol (MEEE) and 2-(2-(2-butoxyethoxy)ethoxy)- ethanol (BEEE) at 415 K. Al-1.0%Sn-1.0%Bi alloy was corroded severely in both BEEE and MEEE, whereas other eight alloys showed no corrosion. The corrosion proceeded under the anodic oxide films through cracks formed in the film. Cathodic polarization in Cu electroplating solution after corrosion suggested that the crack formation during immersion in hot MEEE is due to thermal expansion of the substrate and Sn and Bi containing particles included in the anodic oxide film.

Platinum Nanaflowers on Scratched Silicon by Galvanic Displacement for an Effective SALDI Substrate

Hideya Kawasaski, Teruyuki Yao, Takashi Suganuma, Kouji Okumura, Yuichi Iwaki, Tetsu Yonezawa, Tatsuya Kikuchi, and Ryuichi Arakawa

Chemistry - A European Journal, **16(35)**, 10832-10843 (2010).

We report a new and facile method for synthesizing 3D platinum nanoflowers (Pt Nfs) on a scratched silicon substrate by electroless galvanic displacement and discuss the applications of the Pt Nfs in surface-assisted laser desorption/ ionization-mass spectrometry (SALDI-MS). Surface scratching of n-type silicon is essential to induce Pt Nf growth on a silicon substrate (to obtain a Pt Nf silicon hybrid plate) by the galvanic displacement reaction. The Pt Nf silicon hybrid plate showed excellent SALDI activity in terms of the efficient generation of protonated molecular ions in the absence of a citrate buffer. We propose that the acidity of the Si-OH moieties on silicon increases because of the electron-withdrawing nature of the Pt Nfs; hence, proton transfer from the Si OH groups to the analyte molecules is enhanced, and finally, thermal desorption of the analyte ions from the surface occurs. Signal enhancement was observed for protonated molecular ions produced from a titania nanotube array (TNA) substrate on which Pt nanoparticles had been photochemically deposited. Moreover, surface modification of the Pt Nf silicon hybrid plate by perfluorodecyltrichlorosilane (FDTS) (to obtain an FDTS-Pt Nf silicon hybrid plate) was found to facilitate soft SALDI of labile compounds. More interestingly, the FDTS-Pt Nf silicon hybrid plate acts 1) as a high-affinity substrate for phosphopeptides and 2) as a SALDI substrate. The feasibility of using the FDTS-Pt Nf silicon hybrid plate for SALDI-MS has been demonstrated by using a beta-casein digest and various analytes, including small molecules, peptides, phosphopeptides, phospholipids, carbohydrates, and synthetic polymers. The hybridization of Pt Nfs with a scratched silicon substrate has been found to be important for achieving excellent SALDI activity.

Molten Matrix Sputtering Synthesis of Water-Soluble Luminescent Au Nanoparticles with a Large Stokes Shift

Yuichi Shishino, Tetsu Yonezawa, Koji Kawai, and Hiroshi Nishida

Chemical Communications, **46(38)**, 7211-7213 (2010).

Water-soluble luminescent AuNPs of 1.3 ± 0.3 nm in diameter with a large Stokes shift were facilely synthesized by a new molten matrix sputtering (MMS) method.

Current Activities of OS Process Using Molten $CaO+CaCl_2$

R.O. Suzuki

Proc. 2nd Intern. Round Table on Titanium Production in Molten Salts, suzuki-paper.pdf (2010).

Firstly a direct production of Ti-29Nb-13Ta-4.6Zr biomedical alloy was reviewed. The results of this study indicate that the OS process can be applied to directly produce TNTZ alloy from an oxide mixture, although the standard free energy of oxide formation is largely different in the starting oxides. Secondly the reduction of TiO and $CaTiO_3$ are compared when $CaCl_2$ and CaO mixture was used. The formation of $CaTiO_3$ enhances a sequence of oxide reduction from TiO_2, because $CaTiO_3$ holds high porosity and paths for the salt penetration. Thirdly the reduction of CO_2 gas was reported using yittria stabilized ZrO_2.

Reduction of Oxides Using CaO Electrolysis in Molten Calcium Chloride

R.O. Suzuki

Yohyuhen Oyobi Kouon Kagaku (Molten Salts), 53[1] pp.5-11 (2010).

The molten salt electrolysis of CaO dissolved in $CaCl_2$ melt was conducted among the decomposition voltages of CaO and $CaCl_2$. It can serve a strong reducing atmosphere near the cathode, which is used for the solid oxide reduction to the pure metals. Many oxides were experimentally reduced but some were not recovered as the pure metals probably because they made an alloy with Ca. The mixed oxides were also reduced to form an alloy powder. The subsequent annealing of the reduced powder could homogenize to the same level of the commercial alloy. The liquid oxide (for example, V_2O_5) and gaseous oxide could be reduced. The electrolysis of CO_2 needs a non-reactive anode, and the ZrO_2 solid electrolyte was applied. Fine amorphous or graphite carbon particles were obtained above the molten salt as well as carbon sheet on the anode surface.

Thermoelectric Properties of $Zr_3Mn_4Si_6$ and $TiMnSi_2$

R.O.Suzuki and H.Kozasa

J. Electronic Mater., 39 (9), pp.2017-2022 (2010).

The Seebeck coefficient, electrical resistivity, and thermal conductivity of $Zr_3Mn_4Si_6$ and $TiMnSi_2$ were studied. The crystal lattices of these compounds contain relatively large open spaces, and, therefore, they have fairly low thermal conductivities (8.26 $Wm^{-1}K^{-1}$ and 6.63 $Wm^{-1}K^{-1}$, respectively) at room temperature. Their dimensionless figures of merit *ZT* were found to be 1.92×10^{-3} (at 1200K) and 2.76×10^{-3} (at 900K), respectively. The good electrical conductivities and low Seebeck coefficients might possibly be due to the fact that the distance between silicon atoms in these compounds is shorter than that in pure semiconductive silicon.

Direct Production of Ti-29Nb-13Ta-4.6Zr Biomedical Alloy from Oxide Mixture in Molten $CaCl_2$

S. Osaki, H. Sakai and R.O. Suzuki

J. Electrochem. Soc., No.8, pp.E117-121 (2010).

Ti-29Nb-13Ta-4.6Zr(TNTZ) alloy was successfully produced by co-reduction of oxide mixture, which consisted of TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2. This method uses high reducibility of Ca or Ca-condensed molten salt. Ca was produced by controlled-potential electrolysis of CaO in molten $CaCl_2$ under 3.2 V at 1173 K with carbon anode and Ti cathode. The supplied charge Q was varied in the range of 50~400% of theoretical charge (Q_0) to generate the required amount of Ca to reduce the oxide mixture.

The oxygen concentration of the obtained powder sample decreased monotonously

as the supplied charge increased. 1.37 mass% oxygen could be attained at Q/Q_0 =165% and 1900 mass ppm at Q/Q_0 =323%. X-ray diffraction measurements identified the sample which has low oxygen concentration as the mixture of Ti-based BCC solid solution and a small amount of HCP solid solution. The electron probe microanalysis showed that the composition of this sample was slightly different from the targeted composition due to difference of reduction rate of the component oxides. After sintering at 1300 K for 54 ks, the HCP phase disappeared and the compositional homogeneity was improved within ±3.5 mass% to the targeted composition.

Fabrication of Reusable Aluminum Printing Plate with Conducting Polymer

Tatsuya Kikuchi, Hiroko Shimaguchi, Mikito Ueda, Masatoshi Sakairi, Tetsu Yonezawa, and Hideaki Takahashi

J. Surf. Finish, Soc. Jpn., 61, 652-657 (2010).

A printing plate for gravure printing consisting of five layers of aluminum alloy / anodic oxide film / nickel / polypyrrole / copper was fabricated by anodizing, electro-less plating, electroplating, and electro-polymerization. Nickel layers were first deposited on anodic oxide film-covered aluminum alloy by electro-less plating and electroplating. The polypyrrole layer was then deposited on the nickel layer by anodic polarization in a pyrrole monomer solution. Many copper fine particles were deposited on the polypyrrole-deposited specimen at the initial stage of electroplating in the $CuSO_4$ / H_2SO_4 solution; then a continuous copper layer was obtained through longer cathodic polarization. The copper layer with polypyrrole was removed easily from the nickel layer by pulling with adhesive tape, which suggests that the structure is useful as a reusable aluminum printing plate by copper electroplating and electro-polymerization.

Effects of 2-Buthyne-1,4-diol Additive on Electrodeposited Ni Films from a Watts-type Bath

T. Sakamoto, K. Azumi, H. Tachikawa, K. Iokibe, M. Seo, N. Uchida, Y. Kagaya

Electrochimica Acta 55 (2010) 8570–8578

Structures of Ni films electrodeposited from a Watts-type bath containing 2-buthyne-1,4-diol (BD) were investigated using SEM, cross-sectional SIM, XRD measurement with a pole profiling technique and electrochemical methods for controlling properties of Ni electrodeposits. Preferred orientation of Ni electrodeposits was assigned to potential domains for electrodeposition. Preferred orientation in the higher potential region was (1 1 0) or (1 0 0), that in the middle potential region were (1 1 1) and (3 1 1), and that in the lower potential region was (1 0 0). The growing axis of Ni electrodeposits seems to agree with the speculation from Pangarov's model based on the two-dimensional nuclei theory in the lower overpotential region in which the dominant growing plane is fundamentally determined by crystalliza- tion overpotential related to supersaturation of adatom, although the growth axes of Ni deposits do not always agree with the preferred orientation. For example, preferred orientation of (1 1 0) was assigned to growing (1 1 1) plane which tilts at 55◦ to the substrate. Adsorption of BD affects the structure and mor- phology of electrodeposits via an inhibitory effect related to its surface coverage depending on surface orientation, growth rate and BD concentration in the plating bath.

Application of the Multichannel Electrode Method to Monitoring of Corrosion of Steel in an Artificial Crevice

A. Naganuma, K. Fushimi, K. Azumi, H. Habazaki, H. Konno

Corrosion Science 52 (2010) 1179–1186

Crevice corrosion of iron was evaluated using the multichannel electrode method in which 10 individual working electrodes (WEs) of pure iron were embedded in resin, placed in an artificial crevice in the range from 0.5 mm to 2.0 mm, and immersed in 0.51 mol dm-3 NaCl solution. The WEs were connected to an electronic circuit which allowed galvanic coupling between them and measurement of their individual coupling current or open circuit potential. Time-transient of the spatial distribution of coupling current and open circuit potential showed sequential transition of the coupling current on WEs at the middle position of the crevice from cathode to anode. The WE near the opening of the crevice initially showed a large anodic current, then a decreasing the anodic current corresponding to the current transition of other WEs, and finally a large cathodic current coupled with the other anodic WEs in the crevice. The transition of coupling current was explained by the change in pH and concentration of dissolved oxygen in the crevice. Thickness of the gap of the artificial crevice affected the transition behavior of coupling current distribution. For example, slower current transition with smaller coupling current was found in the case of a narrower gap. Such properties were related to the introduction and consumption of dis- solved oxygen in the crevice solution and the circulation of gap solution from/to the outside of the crevice.

Crevice Corrosion Monitoring of High-Corrosion-Resistive Steels in the Solution Containing Saturated Sodium Chloride at High Temperature Using Multichannel Electrode System

K. Azumi, A. Naganuma

Bulletin of the Society of Sea Water Science, Japan, 64（2010）160-161.

Crevice corrosion of four stainless steels, general stainless steel (SUS316L) and high-corrosion-resistive stainless steels (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, high-corrosion-resistive steels showed typical crevice corrosion behavior, i.e., 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 high-corrosion-resistive steels was not affected by DO, probably due to the establishment of a passive state inside the crevice. (Japanese)

Anisotropic Corrosion of Iron in pH 1 Sulphuric Acid

K. Fushimi, K. Miyamoto, H. Konno

Electrochim. Acta, **55**(24), 7322-7327 (2010).

Anisotropic corrosion behaviour of a single grain of pure iron in 0.05 mol dm^{-3} sulphuric acid (pH 1) was investigated by a simple polarization technique. Both corrosion potential and corrosion current 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. Covalent bonding of Fe and H and coverage of H on Fe seem to play important roles in the HER and anisotropic corrosion behaviour of pure iron.

Influence of Substrate Dislocation on Passivation of Pure Iron in pH8.4 Borate Buffer Solution

Takatoshi Yamamoto, Koji Fushimi, Seiji Miura, Hidetaka Konno

J. Electrochem. Soc., **157**(7), C231-C237 (2010).

The influence of substrate dislocations on the passivation behavior of pure iron in a pH 8.4 borate buffer solution was investigated. Cold-rolling was employed to induce dislocation in the annealed substrate. The dislocation density on the cold-rolled substrate depended on the reduction ratio *Red* and was maximum at *Red* = 60%. The electric charge consumed in the passivation and the passivity-maintaining current increased with an increase in the dislocation density. Electrochemical impedance spectroscopy revealed that the dislocation exposed to the iron surface increased the donor density in the passive film and reduced the charge- transfer resistance for the film aging. It was also demonstrated by radio frequency–glow discharge optical emission spectroscopy that a thick passive film formed on the cold-rolled iron compared with that on annealed iron. These results suggest that substrate dislocations enhance the reactions at the substrate/film interface, resulting in the formation of a highly defective passive film.

Depassivation-repassivation Behavior of a Pure Iron Surface Investigated by Micro-indentation

T. Yamamoto, K. Fushimi, H. Habazaki, H. Konno

Electrochimica Acta, **55**(3), 1232-1238 (2010).

Depassivation–repassivation behavior on a pure iron surface in borate buffer solution was examined under potentiostatic control by a micro-indentation test. Current peaks emerge during both downward and upward drives of the indenter

due to depassivation which is caused by plastic deformation of the substrate but not elastic deformation and repassivation. The total electric charge of the current peaks is proportional to the maximum load. The total electric charge also increases with increase in intermission time of the indentation, indicating that the passive film is ruptured even during stress relaxation. It is estimated from the electric charge balance that 82% and 18% of the film rupture occurs during the downward drive and intermission, respectively, and that no rupture occurs during the upward drive. Furthermore, the film-ruptured area is estimated to be 80% of the plastic deformed surface area. The partial retainment of the passive film on iron suggests that the ductility of the passive film is higher than that of the substrate.

High Capacitance B/C/N Composites for Capacitor Electrodes Synthesized by a Simple Method

H. Konno, T. Ito, M. Ushiro, K. Fushimi, K. Azumi

J. Power Sources, **195**(6), 1739-1746 (2010).

The B/C/N composites were synthesized by a very simple method, that is, carbonization at HTT = 800–1200ºC of the precursor prepared by drying a solution mixture of polyacrylamide and boric acid, followed by boiling in water to remove borate by-products. The amount of insoluble B species in the composite increased linearly from 4.8 to 18.6 mass% with raising HTT. The XRD and FT-IR revealed that turbostratic h-BN started to form at around 1000ºC as a by-product. By XPS, major B and N components in the composite were >B–N< bond, C–B–O type B, pyridinic N, pyrrolic N, and quaternary N. A fraction for >B–N< bond including h-BN in the total B or N components increased with raising HTT and it exceeded 50at% between 900 and 1000 ºC. It was suggested that in the composites formed at HTT > 1000ºC the amounts of h-BN increased, leading to reduction in other B and N components. The S_{BET} was almost unchanged up to 1000ºC, 410–420 $\mathrm{m^2\ g^{-1}}$. Large and broad redox peaks arisen from plural reactions appeared in the cyclic voltammogram (CV) measured in 1 mol $\mathrm{dm^{-3}}$ H_2SO_4 for the composites formed at HTT ≤ 1000ºC. These peaks disappeared in 1 mol dm^{-3} solutions of Na_2SO_4 and Li_2SO_4. By comparing CV with that for C/N composite formed from PAA by the MgO template method, the pseudo-capacitance owing to reactions of >B–N< and C–B–O components with protons was found to be added to commonly observed pseudo-capacitance for nitrogen-doped carbons. The capacitances for the composites formed at 850–950 ºC exceeded 300 F g^{-1} at 2 mV s^{-1} in the acid electrolyte and the retention at 50 mV s^{-1} was 78–80%. The shape of CV in the neutral electrolytes was trapezoid and the current density increased with lowering potential, suggesting adsorption and desorption of Na^+ and Li^+ ions. This was considered to be due to doped nitrogen, indicating the development of pseudo-capacitance. The capacitance per S_{BET} was 0.33–0.74 F m^{-2} and 0.17–0.32 F m^{-2}, larger for lower HTT, in the acid and neutral electrolytes, respectively.

Development of a Low Solution Resistance Type Solution Flow Droplet Cell and Investigation of Its Electrochemical Performance

M. Sakairi, T. Murata, T. Kikuchi, K. Fushimi

ISIJ Int., **50**(10), 1466-1470 (2010).

A solution resistance reduced solution flow type micro-droplet cell with co-axial dual capillary tubes was developed. A Pt counter electrode wire, 50 μm diameter, inserted in the inner capillary tube, successfully reduced solution resistance between the working and counter electrodes. The potentio-dynamic polarization measurements showed the electrochemical performance of developed droplet cell to be very similar to that of traditional macro sized electrochemical cells. The developed droplet cell was applied to obtain line profiles of a current at a constant potential across the surface of for cross-sections of model metal interfaces. The current changed at the model interface between deposited nickel and substrate, and the spatial resolution of the developed droplet cell was reduced with increasing scanning speed of the cell. The results reported in this paper suggest that this

technique would be able to measure differences in corrosion resistance in welded metal components and base metals.

Fabrication of Cu Micro-rods with Co-axial Dual Capillary Solution Flow Type Droplet Cells and Electrodeposition with the Cell

M. Sakairi, Y. Goto, T. Kikuchi, K. Fushimi and H. Takahashi

Electrochemistry, **78**(2), 118-121 (2010).

A new method for mask-less fabrication of metal micro-rods is described. The developed solution flow type droplet cell micro fabrication technique was applied to form Cu micro-rods. The use of an inner capillary tube as a mold during electrodeposition, makes it possible to form Cu micro-rods of about 15 mm length and about 100 μm diameter. The length is controlled by the deposition time. From X-ray analysis and surface observations, the formed Cu micro-rod is polycrystalline and the crystals are very fine. The cross section of the micro-rod was almost circular and the diameter was almost the same throughout its length. This technique also makes it possible to form straight metal structures as well as branched and layered micro-rods. This layered micro-rod fabrication technique can be applied to form resistance controlled micro wires.

Anodic Dissolution of Titanium in Ethylene Glycol Solution Containing Chloride Salt

K. Fushimi, H. Kondo, H. Konno

ECS Transactions, **25**(37) 111-117 (2010).

Anodic dissolution behaviour of titanium in ethylene glycol solution containing chloride salt was examined using a rotating disk electrode. A potential-independent dissolution current flowed depending on the rotation speed, species and concentration of chloride salts. The current controlled by the mass transfer process could flow in concentrated chloride solutions, but decreased with increase in chloride concentration. A smaller current flowed in solution with a high concentration of titanium species, indicating that the diffusion-controlling species are titanium species, not chloride ions. Electrochemical impedance spectroscopy revealed that a titanium chloride salt layer was formed between the titanium substrate and diffusion layer during the mass transfer-controlling anodic dissolution of titanium.

Effect of Cold Rolling on Passive Film on Pure Iron in pH 8.4 Borate Buffer Solution

T. Yamamoto, K. Fushimi, S. Miura, H. Konno

ECS Transactions, **25**(40) 3-15 (2010).

The influence of substrate dislocations on passivation behavior of a pure iron in pH 8.4 borate buffer solution was investigated. Cold rolling was employed to induce dislocation in the annealed substrate. The dislocation density on the cold rolled substrate depended on the reduction ratio (*Red*) and was maximum at *Red* = 60%. The electric charge consumed in the passivation and the passivity-maintaining current increased with increase in the dislocation density. EIS revealed that the dislocation exposed to the iron surface increased donor density in the passive film and reduced charge transfer resistance for the film aging. It was also demonstrated by rf-GDOES that a thick passive film formed on the cold rolled iron compared with that on annealed iron. These results suggest that substrate dislocations enhance the reactions at the substrate/film interface, resulting in the formation of the highly defective passive film.

Formation of Artificial Micro-pits on Al Alloy with PRM and the Localized Corrosion Behavior of the Formed Pits

K. Yanada, M. Sakairi, T. Kikuchi, Y. Oya and Y. Kojima,

Surface and Interface Analysis, 42, 189-193 (2010)

An in situ artificial micro-pit fabrication method with an area selective electrochemical measurement technique was applied to investigate the effect of the geometry of artificially formed pits on their localized corrosion behavior in anodized 1000 series aluminum. This technique enables the fabrication of artificial micro-pits with different aspect ratios (pit depth/pitdiameter) in solutions. The aspect ratios of the fabricated artificial micro-pits in this experiment could be varied from 0.13 to1.83 by controlling the irradiation time of the focused pulsed YAG laser beam. By applying a constant potential to the final laser-beam-irradiated spot in chloride environments, localized dissolution occurred only at the laser beam irradiated area, because the anodic oxide film acted as an insulator. The corrosion current and charge increase with increasing aspect ratio at any applied potential.

The Influence of Initial Surface Conditions on Field Crystallization of Anodic Aluminum Oxide Films Determined by Synchrotron X-Ray Diffraction

M. Sakairi, T. Kikuchi, T. Suda, D. Nagasawa, and M. Sato

Surface and Interface Analysis, 42, 215-22 (2010).

X-ray diffraction measurements were performed using synchrotron radiation at the SPring-8 facility and electrochemical techniques to investigate the effect of polishing methods and storage conditions on the crystal structure of air-formed oxide films and anodic oxide films formed on highly pure aluminum. Storage in an

N2 environment hinders local film breakdown during anodizing, and it was established that the X-ray diffraction measurements showed the presence of a γ-Al_2O_3 in the anodic oxide film formed on mechanically polished (MP) specimens. Formation of γ-Al_2O_3 during anodizing was inhibited by electro-polishing because of the removal of the work-hardened layer that was formed on the MP by electro-polishing. The X-ray diffraction results do not show clear differences in the influence of the polishing method on the crystal structure of air formed oxide film. This is due to the very fast oxidation rate of the air-formed oxide film and very long storage times for the X-ray measurements. The anodic oxide film formed on aluminum, which has a very flat surface, shows color and the color depended on grain orientation. The electrochemical impedance of the MP specimen is slightly lower than that of the mechanically and then electrochemically polished specimen at the middle frequency range. This impedance difference may be due to formation of γ -Al_2O_3 in the amorphous anodic oxide film and the thickness of the film.

Model Cut-edge Formed on Zinc Coated Steels by Laser Machining and Its Corrosion Behavior

M. Sakairi, A. Kageyama and T. Kikuhci,

Corrosion Sci. and Tec., 9, 29-33 (2010)

Laser machining technique, which is used focusing pulse YAG laser beam irradiation was applied to form area ratio controlled model cut-edge on pre painted Zn coated steels. A corrosion behavior of formed model cut-edge was investigated by rest potential measurement in 1 mol m^{-3} NaCl with and without 0.5 kmol m^{-3} H_3BO_4/0.05 kmol m^{-3} $Na_2B_4O_7$. The rest potential showed almost constant value with fluctuations. The amplitude of fluctuations increased with exposed area of steel surface. White corrosion products of zinc oxide and simonkollite was formed after the experiments at the formed model cut-edge.

Aluminum Microstructures on Anodic Alumina for Aluminum Wiring Boards

H. Jha, T. Kikuchi, M. Sakairi, H. Takahashi

ACS Applied Materials & Interfaces, 2 (3), 774–777 (2010)

The paper demonstrates simple methods for the fabrication of aluminum microstructures on the anodic oxide film of aluminum. The aluminum sheets were first engraved (patterned) either by laser beam or by embossing to form deep grooves on the surface. One side of the sheet was then anodized, blocking the other side by using polymer mask to form the anodic alumina. Because of the lower thickness at the bottom part of the grooves, the part was completely anodized before the complete oxidation of the other parts. Such selectively complete anodizing resulted in the patterns of metallic aluminum on anodic alumina. Using the technique, we fabricated microstructures such as line patterns and a simple wiring circuit-board-like structure on the anodic alumina. The aluminum microstructures fabricated by the techniques were embedded in anodic alumina/ aluminum sheet, and this technique is promising for applications in electronic packaging and devices.

Influence of Wettability on Corrosion Resistance of Anodized Aluminum in NaCl Solutions

M. Zheng, H. Jha, M. Sakairi and T. Kikuchi,

Zairyo-to-Kanky, 59, 335-337 (2010)

A simple and effective method is utilized for the fabrication of hydrophobic film on aluminum, and its capability of corrosion resistance is also studied. The surface hydrophobicity of aluminum was developed by anodizing and desiccation treatment. H_3PO_4 solution is considered as a better anodizing solution compared to $H_2C_2O_4$ solution. The water contact angle of anodized samples increases with desiccation time, which indicates that desiccation is an effective method to achieve hydrophobicity of aluminum porous oxide film. The hydrophobic samples show a regular porous surface morphology, and the capillarity of this porous structure probably plays an important role in water-repellent surface. Chemical composition of sample surface before and after desiccation appears almost the same. In 3.5 mass % NaCl solution, the hydrophobic samples suffer little corrosion during a long period of immersion. The rest potential in NaCl solution shows an order: hydrophobic sample > anodized sample > untreated sample, which account for the corrosion resistance improvement of both anodizing and desiccation treatment. The interface area between solution and sample is reduced as the air-valley phenomenon, which may be the reason for corrosion resistance.

Effect of Cations on Corrosion Behavior of Aluminum Alloy in Model Tap Water

K. Otani, M. Sakairi, T. Kikuchi and A. Kaneko

Zairyo-to-Kankyo, 59, 330-331 (2010)

The influence of kind of cations on corrosion behavior of A3003-H24 in model tap water was investigated by immersion corrosion test and galvanic corrosion test. The immersed corrosion behavior is strongly depends on the buffer ability of the solutions, however, the kind of cation does not clearly affect on immersion corrosion behavior. The potential fluctuations and current fluctuations observed in galvanic corrosion tests show good correlation. A coexistence of Na^+ and K^+ in model tap water acts as corrosion inhibitor, while single existence of these ions does not inhibit corrosion of A3003-H24.

Formation of Model Scratch on Pre-painted Coated Steel by Laser Machining and Its Wet/Dry Corrosion Behavior

M. Sakairi, M. Uchida and T. Kikuchi

Ziaryo-to-Kankyo, 59, 379-381 (2010)

A laser machining technique was applied to form S_r controlled model scratch on pre-painted coated steel and its wet /dry corrosion behavior was investigated. In high Sr of both ZN and GL specimens, red rusts are observed on steel substrate at model defects, because zinc corrosion products inhibit sacrificial reaction of zinc. In the case of ZN specimen, dissolution of coated layer start at the rim of scratched area and penetrate to laterally. In the case of GL specimen, zinc rich phase preferentially dissolved. The preferential zinc rich layer dissolution and corrosion products formation cause paint peel off zinc-alloy coating.

Formation of Nanoporous Anodic Oxide Films on Ti-Al Microchannel Walls

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

J. JSEM Special Issue, 10, 210-214 (2010)

Fabrication 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 the body metal and Zn as the 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 nano-porous alumina film was produced by anodic oxidation of the inner wall of the microchannel.

Wet/Dry Cycle Corrosion Behavior of Model Cut-edge Formed on Pre-painted Zinc Alloy Coated Steels by Laser Fabrication

M. Sakairi, A. Kageyama and T. Kikuchi

ECS-Transaction, 25, 71-79 (2010)

Laser machining technique, which used focusing pulse YAG laser beam irradiation, was applied to form area ratio of controlled model cut-edge on pre-painted zinc related coated steels. A corrosion behavior of formed model cut-edge was investigated by wet/dry cyclic corrosion test using 10 mol m^{-3} NaCl solutions in 80 % R.H. atmosphere. In high area ratio zinc specimens, red rust is observed on steel substrate at model cut-edge. The chromate inhibits corrosion of formed model cut-edge on pre-painted zinc coated steels. The behavior of corrosion penetration under the paint depends on composition of coating. In the case of painted zinc-55 mass% aluminum coated steel, zinc rich phase preferentially dissolved. The preferential zinc rich layer dissolution and corrosion products formation cause paint peel off.

Corrosion Resistance Improvement of Aluminum by Hydrophobic Anodic Oxide Film

M. Zheng, H. Jha and M. Sakairi
Proc. of 12th ICAA (2010), Yokohama, 775-780 (2010)

Diminishing surface wettability is an effective method to improve corrosion resistance of aluminum. Various techniques for preparing hydrophobic surface have been reported, most of which use organic coating as the final step. The key point to diminish surface wettability is to form a fine regular surface structure, and the porous type anodic oxide film (PAOF) has nano-pore structure, therefore promising for being utilized to develop hydrophobic surface combined with other treatment. In this study, a hydrophobic surface was prepared on aluminum sheet by constant-current anodic oxidation, followed by desiccation treatment. The surface morphology was investigated by SEM, and chemical composition was analyzed by AES and XPS measurement. The result showed that topside morphology of porous layer was greatly influenced by both desiccation time and temperature, without an evident change in chemical composition. Corrosion behavior of samples was investigated in 0.6 kmol m^{-3} NaCl solution in various immersion time. A decreasing quantum of corrosion products on anodized surface and hydrophobic surface indicated an improvement of corrosion resistance. Potentiodynamic polarization measurement was employed to confirm the corrosion resistance improvement of hydrophobic treatment in the same solution, and the result showed current density of anodized sample decreased more after desiccation process.

Corrosion Behavior of Titanium Oxide Coated Magnesium

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

Proc of 5th ISMCC (2010), Quindao, 277-282 (2010)

A liquid phase deposition method, LPD, can form oxide from aqueous solutions. The LPD was applied to form corrosion resistant titanium oxide film on magnesium. The corrosion behavior of oxide films formed on magnesium was observed by immersion corrosion tests and electrochemical tests in NaCl solutions. The structure of formed film was also examined by transmission electron microscope (TEM), and chemical composition was examined by Raman spectroscopy and Rutherford backscattering spectrometry (RBS). TEM, Raman spectroscopy and RBS showed that formed oxide films were anatase TiO_2 and the thickness was less than 2 μm. When magnesium without oxide film was dipped in NaCl solution, dissolution is observed everywhere on the surface, while magnesium with oxide film initially shows no corrosion and even after 86.4 ks corrosion is very limited.

Microstructure of Hydrophobic Alumina Film and Its Corrosion Resistance Analysis

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Porous type anodic oxide film (PAOF) is one type of alumina film, which has been studied in many scientific fields such as catalysis, template, insulator, and luminescence. Besides, it is a similar structure to many natural or artificial hydrophobic surfaces that PAOF shows evident roughness with numerous micro-pores on it. However, the as-anodized oxide film contains certain amount of hydroxide or water molecular so that it basically shows hydrophilic property. In this study, heating desiccation and room temperature desiccation were utilized to develop the hydrophobicity of PAOF. Its microstructure and chemical composition was analyzed by SEM and XPS. The water contact angle of anodized samples in H_3PO_4 solution was greatly increased by the desiccation treatment at 353 K and 373 K. At both desiccation temperature, the water contact angle was also increased with time, reaching a maximum of 116° after 1728 ks. From SEM measurement, a regular porous layer with an average pore diameter of 176 nm was observed on the desiccated sample. After both desiccation treatments, chemical composition of oxide film remained almost same as the as-anodized oxide film. A dynamic analysis was applied to explain the situation of interface between water droplet and porous layer, and the relationship between pore diameter and water contact angle was discussed. Rest-potential of different samples were measured in NaCl solution, and the result accounts for corrosion resistance improvement of both anodizing and desiccation treatment. Based on the interface model, the corrosion resistance of hydrophobic PAOF could also be explained.

Alkali Leaching of Ni-Al Microchannel Lining Layers

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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 Al_3Ni or Al_3Ni_2 lining layer. The Al concentration of the lining layers was successfully decreased by alkali leaching.

Anodic Oxidation of the Inner Wall of the Microchannel Formed in Sintered Aluminum Body

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Fabrication 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 the body metal and Zn as the 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 nano-porous alumina film was produced by anodic oxidation of the inner wall of the microchannel.