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CURRENT ACTIVITIES and PRESENTATIONS

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

Research programs in progress are as follows:

(1) New corrosion resistive coating consisting of conductive polymers

A conductive polymer coating was applied to corrosion prevention of carbon steels and zinc-alloy coated steels.

A bilayered polypyrrole (PPy) film doped by molybophosphate (MoP) ions at the inner layer and by organic ions at the outer layer was electrochemically formed on the carbon steel plate in aqueous solution containing pyrrole monomer. The MoP ions doped in the inner layer facilitates formation of stable passive oxide film between the PPy layer and substrate steel. The large organic anions doped in the outer layer suppresses leaching of the MoP into aqueous solutions. The corrosion protection of the layer was tested by immersion of the PPy-coated steel in aqueous NaCl solution. The passivity of the steel was maintained for time period longer than 100 h, where appreciable corrosion was not observed.

The PPy film was also prepared on Zn or Zn-Al alloy coated steels from tartrate solution containing sodium molybdate and pyrrole monomer. During the constant current polymerization, a salt layer consisting of zinc or Al tartrate is initially formed on the substrate and then the PPy film is polymerized. The coating of PPy effectively maintains the Zn and Zn-Al alloy coatings at the passive state by an immersion test in NaCl aqueous solution.

(2) Monitoring of corrosion products on model galvanic couple of Zn-Fe by Raman spectroscopy

Corrosion products on zinc or zinc-aluminum alloy coating on steels exposed in humidified air were studied by in-situ Raman spectroscopy. The Zn or Zn-Al alloy coating was galvanically coupled with the bare steels. At the presence of NaCl precipitate, zinc-hydroxy carbonate and zinc-hydroxy chloride is observed on both surface of zinc layer or zinc alloy layer and bare steel. The formation of zinc-hydroxy chloride depends on concentration of $ZnCl_2$ in aqueous layer in which Zn^{2+} was initially formed from a reaction of $Zn \rightarrow Zn^{2+} + 2e$ coupled with oxygen reduction on bare steel surface. The coupling with the bare surface accelerates the corrosion of Zn or Zn-Al alloy coatings.

(3) Corrosion and passivation of Nd-Fe-B permanent magnets

Passivation of a NdFe-B permanent magnet was studied in neutral borate solution and phosphate solutions. Thickness of the passive oxide film was measured by in-situ ellipsometry. The passive oxide film linearly grows with increasing anodic potential. From the thickness growth during constant potential it is found that the film growth is followed by the ionic migration mechanism under high electric field proposed by Cabrera and Mott. From an in-depth elemental profile by GD-OES, the passive film is found to preferentially composed of iron oxide or hydroxide. Boron and neodymium are, respectively, concentrated at the surface on the oxide film and at the inner layer in the oxide film. The similar passivation was also observed in the neutral phosphate solution.

(4) Electrodeposition of Zn-Al alloy in chloride molten salt

Zn-Al alloy was electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $ZnCl_2$ for corrosion protection of steel. The electrodeposition was performed by constant potential electrolysis with various potential. The Zn content in the alloy drastically increases from 4 to 90 at% at potential from -15 to -10 mV (vs. Al/Al(III)).

(5) Electrodeposition of Bi-Sb-Te and Sb-Te alloys in chloride molten salt

Bi-Sb-Te alloys were electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $BiCl_3$, $SbCl_3$, and $TeCl_4$ at 423K. Stable deposition of pure Bi and pure Te were not obtained by the electrolysis, because electrodeposited Bi and Te dissolved into the molten salt immediately. Sb-Te alloy also was successfully electrodeposited in the melt containing $SbCl_3$, and $TeCl_4$. The composition of Bi-Sb-Te and Sb-Te depended on concentration of Sb ion in electrolyte between 5 and 9 mM.

(6) Recovering of Al from Al alloy by filtering through Zn-Mn composite oxide

To remove the Mg content in Al alloy, a reactive filter of $ZnMn_2O_4$ synthesized from the used dry battery was prepared. Metallic Mg reacted with $ZnMn_2O_4$ to produce $MgMn_2O_4$ at 1073K. Mg concentration in the Al alloy decreased from 6 to 1 at% after the filtration.

(7) Evaluation of Rust layer on Weathering steels

The weathering steel can be used for bridges without any surface finishing. The weathering steels are protected by a stable rust layer with color of dark brown. The life period of the steels depends on the property of the rust layer. The rust layer on the steels were studied by weighing amount of water vapor absorbed in the rust and the electric conductance changing with the absorption. The amount of the water adsorbed is saturated in a few hours and the water absorption induces a great change of the conductance. The conductance change may be responsible to the protection capability of the rust layer.

(8) Long-term Stability of the Co-Pt or Co-Pd Cathodes of Polymer Electrolyte Fuel Cell

Co-Pt and Co-Pd alloy electrodes were studied for an efficient cathode of oxygen reduction in FEFC. The oxygen reduction current was measured and compared between the alloy electrodes with different composition. The Co alloy electrodes are more efficient than Pt or Pd electrode. The alloy electrodes with composition higher than 50 mol% of Co reveals relatively high corrosion rate in 0.5 M H_2SO_4 which is a simulated electrolyte of the cathodic part

Other Activities

Assoc Prof. Ueda attended the 4th International Society of Electrochemistry spring meeting, Singapore, April 17-20, 2006, and presented a paper entitled by "Electroplating of intermetallic compounds of Al, Cr, and Ni in $AlCl_3$-NaCl-KCl molten salt".

Facilities and Capabilities

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light.
Potential Modulation Reflectance: Wavelength region from 350 to 800 nm.
Raman Scattering Spectrometer: JASCO R-800T, triple type of spectrometer equipped with an Argon gas laser of 2W power.
FT-IR Spectrometer: JASCO FT/IR 550 equipped with MCT detector for in-situ measurement of corrosion layers on metals.
QCM system for in-situ gravimetry of surface layer on metals.
Electrochemical AC Impedance: NF Circuit Design 5020 FRA equipped with a specially designed potentiostat.
Spectrophotometer: JASCO V-520 in a wavelength region from 200 to 900 nm.
Electrochemistry apparatuses.
Optical Microscopy
Electrochemical Corrosion-Rate Monitor System.

Presentations

Removal of alloyed elements from liquid aluminum scrap by filtering, H. Ryu, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Hokkaido University, Sapporo, January 19-20, 2006.

Corrosion of Nd magnets in NaCl solution, Y. Nunoko and T. Ohtsuka Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Hokkaido University, Sapporo, January 19-20, 2006.

Raman spectroscopy of corrosion products on model cut edge of Zn coated steel, Y. Abe, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Hokkaido University, Sapporo, January 19-20, 2006.

Selective electrodeposition of Bi-Te alloy in chloride molten salt, H. Ebe, M. Ueda, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, January 31-Feuruary 1, 2006.

Formation condition of polypyrrole film on zinc electrode, S. Tsuchiya, M. Ueda, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, January 31-Feuruary 1, 2006.

Electrochemical behavior of the additive on Cu plating process, M. Tasuda, T. Sasaki, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, January 31-Feuruary 1, 2006.

Development of PPy-PMo_{12} and PPy-NDS double layer coating for corrosion protection of steel, D. Kowalski, M. Ueda and T. Ohtsuka, The 113th Annual Meeting of Surf. Finish. Soc. Jpn., Toyo University, Kawagoe, March 15-17, 2006.

Raman spectroscopy for the corrosion products on model cut edge surface on Zn coated steel, Y. Abe, T. Ohtsuka, and M. Ueda, Jpn Inst. Metals 2006 Spring Meeting, Waseda University, Tokyo, March 21-23, 2006.

The oxide film exhibiting a high corrosion resistance on steels, T. Ohtsuka, The 151th Meeting of ISIJ, Waseda University, Tokyo, March 21-23, 2006.

Corrosion protection of steels by a conductive polypyrrole coating doped with $PMo_{12}O_{40}^{3-}$ ions, T. Ohtsuka and M. Iida, The 151th Meeting of ISIJ, Waseda University, Tokyo, March 21-23, 2006.

Formation conduction and protection capability of polypyrrole film on zinc electrode, T. Ohtsuka, S. Tsuchiya and M. Ueda, The 73rd. Meeting of Electrochemical Society of Jpn, Tokyo Metropolitan University, Tokyo, April 1-3, 2006.

Co-deposition of Bi-Te-Sb alloys from chloride molten salt, M. Ueda, H. Ebe, and T. Ohtsuka, The 73rd Meeting of Electrochemical Society of Jpn, Tokyo Metropolitan University, Tokyo, April 1-3, 2006.

Electroplating of intermetallic compounds of Al, Cr, and Ni in $AlCl_3$-NaCl-KCl molten salt, M. Ueda, H. Kigawa, and T. Ohtsuka, 4th International Society of electrochemistry spring meeting, Singapore, April 17-20, 2006.

Corrosion protection of steel by bilayered polypyrrole coatings, D. Kowalski and T. Ohtsuka, Zairyo-to-Kankyo 2006 Annual Meeting, Tsukuba International Conf. Hall, Tsukuba, May 16-18 2006.

Reduction of alloy elements in liquid aluminum scrap using a ceramics filter, H. Takahashi, T. Shigyo, T. Akazawa, M. Ueda, Y. Shibata, T. Takashima, The 160th meeting of molten salt committee, Hokkaido University, Sapporo, June 1, 2006

Measurement of anodic passivation films on Nd permanent magnet by ellipsometry. M. Nunoko and T. Ohtsuka, Hokkaido Branch 2006 Meeting of Chemical Society of Japan, Muroran Inst. of tech., Muroran, July 22-23, 2006.

Formation of conductive polypyrrole film for corrosion protection of zinc, S.

Tsuchiya, M. Ueda, and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Hokkaido University, Sapporo, July 27-28, 2006

Corrosion products on model cut edge of Zn-5%Al and Zn-12%Ni coated steel in the presence of NaCl, Y. Abe, M. Ueda and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Hokkaido University, Sapporo, July 27-28, 2006

Electroplating of Al-Zn alloy in chloride molten salt, A. Munekata, M. Ueda, and T. Ohtsuka, The 114th Annual Meeting of Surf. Finish. Soc. Jpn., Sapporo, October 13-14, 2006

Optical Characterization of Very Thin Films of Passivation on Nickel in Aqueous Solution, M. Iida and T. Ohtsuka, Intern. Symp. on Adv. Fluid/Solid Science and Technology in Experimental Mechanics, Sapporo, Sept. 11-14, 2006,

Potential Modulation Reflectance of Manganese Tetraphenylporphyrin Derivatives Assembled on Gold Electrodes, T. Ohtsuka, Taku Yamada, and M. Nango, The international Session in the 59 th Divisional Meeting on Colloid and Surface Chemistry, The Chemical Society of Japan, Hokkaido University, Sapporo, Sept.. 13-15, 2006

Corrosion Prevention of Steel by Using Conductive Polypyrrole Coating, D. Kowalski, M. Ueda, and T. Ohtsuka, The international Session in the 59 th Divisional Meeting on Colloid and Surface Chemistry, The Chemical Society of Japan, Hokkaido University, Sapporo, Sept. 13-15, 2006,

Electroplating of Al-Zn alloy in $AlCl_3$-NaCl-KCl molten salt, A. Munekata, M. Ueda, and T. Ohtsuka, fall meeting of ECSJ 2006, Dohshisya University, Kyoto, September 14-15, 2006

Corrosion products of zinc coated steels exposed in atmosphere in the presence of NaCl, Y. Abe, M. ueda, and T. Ohtsuka, The 53rd Discussion Meeting of

Zairyo-to-Kankyo, Akita University, Akita, Sept. 27-29, 2006.

Anodic passivation film on Nd permanent magnet bu ellipsometry, Y. Nunoko and T. Ohtsuka, The 53rd Discussion Meeting of Zairyo-to-Kankyo, Akita University, Akita, Sept. 27-29, 2006.

Corrosion Prevention of Steel by Bi-layered Polypyrrole Coatings, D. Kowalski, M. Ueda, and T. Ohtsuka, The 53rd Discussion Meeting of Zairyo-to-Kankyo, Akita University, Akita, Sept. 27-29, 2006.

Polypyrrole coating for corrosion prevention of steels, D. Kowalski, 2006 Young Scientist Seminar of Corrosion Branch of ECS Japan, Tokyo Inst. Tech., Oct. 23, 2006

Iron rust and passivation of iron, T. Ohtsuka, The 30th Discussion Meeting of Electrochemical Technology, Kyodai Kaikan, Kyoto, Nov. 23-24, 2006.

Electrodeposition of Al-Zn alloy in $AlCl_3$-NaCl-KCl molten salt using constant potential electrolysis and potential pulse electrolysis, A. Munekata, M. Ueda, T. Ohtsuka, The 38th Symposium on Molten Salt Chemistry, Tokyo University of Science, Noda, November 28-29, 2006

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Miss. Kirsten A. Lill, Max-Planck Institute for Iron Research, Germany, stayed as a foreign researcher (Short-Stay Researcher from Europe or Northern America) of JSPS from January to March. In April, Dr. Hiroaki Habazaki has become a professor of the laboratory as the successor of Prof. Masahiro Seo who retired in March. Simultaneously Dr. Kazuhisa Azumi has moved to Advanced Materials Chemistry Laboratory as the associate professor.

The research activities of the laboratory are directed to the development of advanced oxide films and nanomaterials utilizing anodic oxidation process. We are also interested in micro-electrochemistry and 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) Formation of barrier-type anodic oxide films on niobium 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 control of the anodic film 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.

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

We have successfully developed self-organized porous anodic films on Ti-Si alloys, niobium and aluminum in hot phosphate-glycerol electrolyte. The morphology of the anodic films formed in this electrolyte resembles the traditional anodic alumina films formed in aqueous acid electrolytes. The characteristic features of the anodic films formed in the hot non-aqueous electrolyte are the absence of the phosphate anions in the anodic films, which are usually incorporated in the anodic films formed in aqueous electrolytes and low concentration of carbon species in the anodic films despite the use of the organic electrolyte.

(3) 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. Sparking during anodizing in alkaline solutions containing aluminate ions results in the formation of thick oxide, several tens micrometers, composed mainly of Al_2TiO_5 with high hardness. Spark anodizing has been also applied to magnesium alloys to improve the corrosion resistance.

(4) Preparation of carbon nanocarbons using porous anodic alumina and etched aluminum foil templates

Porous anodic alumina developed on plain aluminum foils and etched aluminum foils have been used as template materials for the preparation of carbon nanofilaments. We have prepared successfully carbon nanofilaments and brush-type nanocarbons by liquid phase carbonization of polymers in the templates. Superior high rate capability of the carbon nanofilaments as anode materials for lithium ion batteries has been found. It has been also found that the nitrogen-containing nanocarbons prepared by this template technique shows high capacitance for electrochemical capacitors, probably due to pseudo-capacitance of nitrogen species in addition to the electric double layer capacitance.

(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 us to obtain depth profiles precisely and quantitatively.

(6) Current Transients of Passive Iron and Stainless Steel during Micro-indentation in Solution

Micro-indentation tests of passive iron and stainless steel in aqueous solutions were carried out to investigate the kinetics and mechanism of depassivation and repassivation. Drives of a conical diamond or sapphire micro-indenter downward to and upward from the passive surface, a couple of anodic current peaks emerge. The first current peak spiked during loading was responsible for partial exposure of substrate metal to the solution due to rupture of the passive film during the indenter tip penetrated. The second peak emerged during unloading when elastic deformation recovered, which was ascribed to repair at the ruptured sites. Appearance of current peaks was investigated for understanding influence of chloride ion in solution and corrosion resistance of stainless steels. The model for a series of rupture and repair processes of the passive film by micro-indentation was proposed to discuss the current transients.

(7) Development of Flowing-electrolyte Type Scanning Droplet Cell Technique and Application of Corrosion Potential Profiling of Aluminum Alloy Brazing Sheets

A new droplet cell technique was developed to study micro-electrochemistry on functional graded materials. It was modified so-called scanning droplet cell (SDC) technique in which the small electrolyte droplet was hung from a capillary tube including counter and/or reference electrodes and scanned on the measuring localized surface which was operated as a working electrode. In the developed technique, i.e., flowing electrolyte-type scanning droplet cell (f-SDC), a coaxial dual-capillary was employed to enable changing electrolyte to fresh one continuously and avoiding contamination by dissolution of products from the measuring surface or deposition of reactants to the surface. The technique of f-SDC was applied for the investigation of the corrosion potential profiles of aluminum alloy brazing sheets which were used for a heat exchanger of automobiles. It was revealed that the potential distribution was depended on that of composition in the cross-section of the brazing sheet. Diffusion of Zn was strongly correlated with the potential gradient from sacrificial anode to core layers. A lateral resolution of the potential profile attained was 15 µm.

(8) Scanning Electrochemical Microscopy of Corrosion of Light Weight Ferritic Steel in Active or Passive State

The alloy Fe7.5Al7Cr is a light weight ferritic steel with a strong anisotropic dissolution behaviour. This steel shows a good passivation behaviour in which the passive film forms in both cases in air and through anodization. The film is composed of both aluminium oxide and chromium oxide. Electron back scatter diffraction (EBSD) allowed determining the map of crystallographic orientation of the polycrystalline material. This map coincides nicely with the optical image of the material. The dissolution kinetics of this steel was investigated in the active or passive state by means of a scanning electrochemical microscope (SECM). Iron dissolving from the steel was directly utilized by the Pt tip of the SECM to measure the amount of locally dissolving material. It is shown that the difference in dissolution rate between various crystallographic orientations is only marginal. Grain boundaries on the other showed a higher activity as compared to the grains themselves.

Other Activities

In August, Prof. H. Habazaki, Dr. K. Fushimi, Mr. T. Ogasawara, Mr. Y. Oikawa, Mr. M. Kiriu and Mr. T. Yamamoto participated in the 57th Annual Meeting of the International Society of Electrochemistry, Edinbourgh, UK, and Prof. Habazaki and Dr. Fushimi presented the papers entitled “High Rate Capability of Platelet Structure Carbon Nanofibers as Anode Materials for Lithium Ion Batteries” and “Application of Segmentalaized Electrode System to Corrosion Monitoring”, respectively.

The following foreign scientist visited this laboratory: Dr. Stefano Mischler, Institute of Materials, Ecole Polytechnique FéSérale, Lausanne, Switzerland, from September 19 to 20.

Presentations

T. Yamamoto, K. Fushimi, K. Azumi, M. Seo; Indent Rate Dependence of Current Transient Observed During Micro-indentation, The 53rd Annual Meeting of Electrochem. Soc. Jpn., Hachiohji, Apr. 1-3, 2006.

K. Fushimi, K. Azumi, M. Seo; Development of Flowing-electrolyte Type Micro Droplet Cell Technique and Its Application to Local Electrodeposition, ibid.

H. Habazaki, M. Kiriu, M. Hayashi, H. Konno; Lithium ion insertion and de-sorption properties of carbon nanofibers prepared using porous anodic alumina template, 43rd Research Meeting of the Solid State Ionics Society of Japan, Sapporo, June 23, 2006

K.A. Lill, K. Fushimi, A.W. Hassel, M. Seo; Investigations on the kinetics of single grains and grain boundaries by use of Scanning Electrochemical Microscopy (SECM), 6th International Symposium on Electrochemical Micro and Nano System Technology, Bonn, Germany, Aug. 22-25, 2006.

M. Kiriu, H. Habazaki, H. Konno; High Rate Capability of Platelet Structure Carbon Nanofibers as Anode Materials for Lithium Ion Batteries, The 57th Annual Meeting of the International Society of Electrochemistry, Edinbourgh, UK, Aug.27-Sep.1, 2006.

M. Kiriu, H. Habazaki, H. Konno; Lithium Insertion/Extraction Characteristics of Carbon Nanofibers Formed from PAA Using Porous Template, ibid.

T. Ogasawara, H. Habazaki, H. Konno, K. Shimizu, S. Nagata; Role of Foreign Species in Nucleation and Growth of Crystalline Oxide in Amorphous Anodic Niobia, ibid.

Y. Oikawa, H. Habazaki, H. Konno; Formation of Porous Alumina Films in Hot Glycerol Solutions Containing Phosphate, ibid.

K. Azumi, K. Fushimi, A. Naganuma; Application of Segmentalaized Electrode System to Corrosion Monitoring, ibid.

K. Fushimi, K. Azumi, M. Seo; A Numerical Model of Rupture and Repair of Passive Film on Iron in pH 8.4 Borate Buffer during Micro-indentation, ibid.

T. Yamamoto, K. Fushimi, K. Azumi, M. Seo; Current Transients from Type-185N Stainless Steel Observed during Micro-indentation Test in pH 8.4 Borate Buffer Solution, ibid.

K.A. Lill, K. Fushimi, A.W. Hassel, M. Seo; The kinetics of single grains and grain boundaries by SECM, The 4th Workshop on Scanning Electrochemical Microscopy (SECM), Falcade, Italy, Sep.3-6, 2006.

M. Nakajima, K. Fushimi, H. Habazaki, K. Toyotake, Spark anodizing of titanium alloys for improvement of wear resistance, Kyotanabe, The 2006 Annual Meeting of Electrochem. Soc. Jpn., Kyotanabe, Sep. 14-15, 2006.

T. Ogasawara, H. Habazaki, K. Fushimi, H. Konno, K. Shimizu, S. Nagata, T. Izumi, Suppression of field crystallization of anodic niobia by addition of silicon, ibid.

K. Fushimi, K. A. Lill, A. W. Hassel, M. Seo; Difference of Reaction Rate on between Single Grains and Boundary Observed by Scanning Electrochemical Microscopy, The 53rd

Annual Meeting of Jpn. Soc. Corrosion Eng., Akita, Sep. 27-29, 2006.

F. Sato, M. Sakairi, K. Fushimi; Localized Surfacial Electrodeposition by Flowing Micro-electrolyte Droplet Cell, ibid.

T. Nakayama, M. Sakairi, K. Fushimi; Localized Electrochemical Measurement of Welded Materials by Flowing Micro-electrolyte Droplet Cell, ibid.

M. Kiriu, H. Habazaki, K. Fushimi, H. Konno; Rate capability of carbon nanofilaments prepared by liquid phase carbonization for lithium ion batteries, The 114th Annual Meeting of Surf. Finish. Soc. Jpn., Sapporo, Nov. 13-14, 2006.

M. T. Tanvir, K. Fushimi, H. Habazaki, K. Shimizu; "Structure and Dielectric Properties of Anodic Films Formed on Ti-Si Alloys", ibid.

T. Yamamoto, K. Fushimi, H. Habazaki, M. Seo, S. Tsuri, T. Adachi; Current Transients Observed during Repeated Micro-indentation of Passive Iron Surface in pH8.4 Borate Solution, ibid.

A. Naganuma, K. Fushimi, K. Azumi, H. Habazaki; Development of Multi-channel Electrode Technique and Its Application to Crevice Corrosion Monitoring, ibid.

M. Seo, Y. Kurata, D. Kawamata, K. Fushimi, M. Chuba; Discontinuity in the Load-Depth Curve of Single Crystal Ta(100) Anodized, ibid.

M. Kiriu, H. Habazaki, K. Fushimi, H. Konno; Characteristics of carbon nanofilaments prepared by liquid phase carbonization of polyacrylamide in porous template as electrode for lithium ion batteries, The 33rd Annual Meeting of the Carbon Society of Japan, Sapporo, Dec. 6-8.

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Research work at "Laboratory of Interface Micro-Structure Analysis (LIMSA)" directs toward 1) the development of micro-devices by aluminum-anodizing / laser-irradiation / AFM probe-processing, 2) evaluation of dielectric properties of anodic oxide films on Al and Nb, and 3) establishment of localized corrosion mechanism of coated steels, titanium and aluminum alloys.

The topics of investigation are in the following:

(1) Cathodic polarization of niobium covered with anodic oxide films

Niobium covered with anodic oxide films were cathodically polarized in a neutral borate solution, and cyclic voltammetry (CV), electrochemical impedance spectrometry (EIS), and glow discharge optical emission spectrometry (GDOES) were carried out to examine the change in the structure of anodic oxide films by cathodic polarization. In the cathodic cycle of CV, cathodic current increased as the potential becomes lower beyond –0.7 V (vs. Ag / AgCl) on each anodized specimen, while no current was observed in the anodic cycle. The cathodic current was lower on the specimens with thicker oxide films.

It was found from GDOES that hydrogen is enriched at the interface between oxide film and the metal substrate after a long cathodic polarization. The EIS suggested that the hydrogen diffuses across the film during cathodic polarization, and that the hydrogen diffusion coefficient become higher at lower potentials.

(2) Micro-patterning of anodic oxide films on aluminum by laser irradiation and electroless metal plating

Aluminum specimens covered with porous anodic oxide films were immersed in Alizarin red-S solution containing small amounts of Pd^{2+} ions, and then immersed in boiling distilled water for 15 min. The former treatment allows the adsorption of dye-stuff and Pd^{2+} ions on the inner walls of porous anodic oxide films, and the latter treatment enables the formation of highly crystalline hydroxide on the outermost surface and pore-filling with hydroxide. Irradiation of a pulsed Nd-YAG laser with accurate control of the laser energy and scanning rate caused only the highly crystalline hydroxide at the outermost parts of the oxide film to be removed, leading to the exposure of Pd^{2+} adsorbed at the of micro-channels and micro-chambers on the oxide film. The subsequent electroless Ni-P plating resulted in the Ni-P deposition on the channels and chambers.

(3) Copper deposition at selected area on aluminum covered with anodic oxide films

Copper deposition at selected area on aluminum alloys covered with anodic oxide films were attempted by laser irradiation and electro-plating. Aluminum alloy specimens covered with anodic oxide films were irradiated with a pulsed Nd-YAG laser to form aluminum substrate-exposed spots with 100 μm diameter and 300 μm interval in nickel plating solutions. After laser irradiation, the specimen was cathodically polarized to deposit nickel on the substrate-exposed spots, and then subjected to electroplating in copper plating solutions. Copper was observed to be deposited on the nickel deposits, and grew radially with the electroplating period, eventually leading to a continuous layer on anodic oxide films. The copper layer deposited on anodic oxide films could be removed easily mechanically.

(4) Initial stage of localized corrosion on HAP coated Ti in vitro by photon rupture method (PRM)

A photon rupture method, oxide film removed by focused pulsed Nd-YAG laser beam irradiation, applied to investigate localized repair of passive oxide films of HAP coated titanium. To optimize formation condition, it is possible to form HAp layer, which may has porous structure on porous type anodic oxide film formed titanium. The corrosion resistance of titanium anodic oxide film does not change by HAp coating, however NaOH treatment significant affects on corrosion resistance of the film. The peak current of HAp coated titanium after laser irradiation lower than that of only anodized titanium.

(5) Formation of Al-Nb composite oxide films on aluminum by electrophoretic sol-gel coating and anodizing

Aluminum specimens were coated with Nb_2O_5 films by a sol-gel electrophoretic method, and then anodized galvanostatically in a neutral boric acid / borate solution. Anodizing of Nb_2O_5 film-coated specimens lead to the formation of anodic oxide films consisting of an outer Al-Nb composite oxide layer and an inner alumina layer. Parallel capacitance of anodic oxide films obtained thus was appreciably larger than that obtained on specimens without any coating. The above treatment was applied for the aluminum foils with rough surface formed by DC-etching, and beneficial effects on the capacitance was not obtained, maybe due to uneven coating of Nb_2O_5 on the walls of tunnel pits.

(6) Fabrication of solid type electrolytic capacitors using Al / Nb-composite oxide films on aluminum

Al / Nb-composite oxide films were formed on aluminum by MOCVD and anodizing, and immersed in iron para-toluenesulfonate / buthanol solutions with

50 % water contents to examine the deterioration of the anodized specimen. The Al / Nb-composite oxide film was found to be much more stable in the solution than anodic oxide films formed by anodizing of electropolished aluminum. Proto-type of solid electrolytic capacitances were fabricated by attaching poly-ethylenedioxythiophene (PEDT) as a solid elctrolyte on Al / Nb-composite oxide film covered aluminum. They showed a high capcitance, but relatively low breakdown voltage.

(7) Crack formation of platinum layer during electro-plating

Platinum electroplating was attempted on copper specimens in a $Pt(NH_3)_2(NO_2)_2$ / CH_3COONa / Na_2CO_3 solution to examine the effect of additives on the crack formation in platinum layers. Deposition rate of platinum on Copper during electroplating in this solution is proportional to current density and the current efficiency for platinum deposition is about 50 %. Cracks are formed throughout Pt layer when it become thicker than 20μm, and the threshold thickness does not depend on current density. Addition of saccharin in the solution leads to the formation of many micro-cracks, which do not reach the substrate.

(8) Electrochemical Behavior of Welded Stainless Steels with Micro Droplet Cell

The flow type micro droplet cell was applied to electrochemical behavior of welded stainless steels. The corrosion resistance of the weld metal is much higher than those of the base metal and HAZ that are almost same in both measurement with macro cell and micro droplet cell. At constant voltage, current of the base metal decreases with time, whereas that of HAZ remains large value oscillating. The structure of base metal is acicular, whereas the structure of HAZ is finer, which is likely consistent with the electrochemical behaviors.

(9) Fabrication of micro-actuators by laser irradiation and electro-polymerization

This is an experimental work subsequent to the efforts for last three years, where micro-actuators with acrylic acid resin / gold / poly-pyrrole three-layer cylindrical structure was attempted to fabricate by aluminum anodizing / laser irradiation / Au deposition / acrylic acid resin deposition / detachment of Au-resin two layer structure / deposition of poly-pyrrole layer. In this investigation, experiments were carried out to make the fabrication process simpler and to improve the performance of actuators. Successive steps of anodizing, laser irradiation, Au deposition, deposition of poly-pyrrole layer, and detachment of Au-poly-pyrrole two layer structure were examined. In the detachment step, the electro-conductivity of poly-pyrrole was lost during immersion in a NaOH solution on open circuit, while it remained high during immersion of the specimen connected with Pt. The mobility of ribbon-type Au-poly-pyrrole actuators fabricated by the new process described above was higher than that by the old process.

(10) Local deposition of acryl acid / melamine resin on aluminum by AFM probe processing and electro-phoretic deposition

Aluminum foils covered with thin barrier type anodic oxide films were set at the bottom of an electrochemical cell on the stage of atomic force microscope (AFM) and then solutions containing small particles of acrylic acid-/ melamine-resin were added in the cell. Under cathodic polarization in the solution, the specimen was scratched by a diamond probe of AFM to carve the surface. The depth of channels formed by scratching increased with the repetition time, but was independent of the force of AFM probe. Anodic polarization of the specimen after scratching in the same solution as used for scratching allowed the resin to be deposited only at the area that the film had been removed.

(11) Local Electro-deposition of 2D and 3D Ni structure on cupper with Micro Droplet Cell

The flow type of micro droplet cell was applied to form Nickel 2D and 3D micro rods on cupper. The nickel 2D structure on cupper substrate can be formed by electrochemically. To optimized deposition condition and stage moving speed, it is possible to form nickel micro rods, which have 2 mm height and 100 μm in diameter. The deposition rate is about 0.13 $\mu m\ s^{-1}$.

(12) Corrosion behavior of anodized aluminum in dilute chloride ion containing solutions

The effect of Cl^- concentrations and effect of Cu^{2+} ion on localized corrosion of aluminum were examined by galvanic corrosion test and potentio dynamic polariztion test in 0.5 kmol m^{-3} H_3BO_4 / 0.05 kmol m^{-3} $Na_2B_4O_7$（pH 7). Localized corrosion potential increases with decreasing Cl^- concentrations. After localized corrosion occurs, galvanic potential and current change with fluctuations and the galvanic current change correlate closely with galvanic potential change. Addition of Cu^{2+} ions, rest potential changes to positive direction. This behavior can be explained by changes of cathodic reaction and rate.

(13) Corrosion behavior of aluminum alloys in artificial pits formed with photon rupture method.

A artificial micro pits was formed by photon rupture method on aluminum and investigated influence of pits geometry on localized corrosive behavior in artificial pit of 1070 aluminum alloy in 0.5 kmol m^{-3} H_3BO_4 / 0.05 kmol m^{-3} $Na_2B_4O_7$（pH 7) with NaCl. It is possible to form artificial pit in 1070 aluminum alloy by continuous Nd:YAG laser irradiation and this technique makes it possible to measure corrosion current at the artificial pit. The current of the artificial pit increases with increasing aspect ratio of pit.

Other activities

In April, Prof. Takahashi and Mr. Jha attended the 8th International Conference on Advanced Surface Engineering in Tokyo, and presented two papers entitled “Fabrication of Micro Dot Arrays of Acrylic Acid Resin on aluminum by AFM Probe” and “Laser Assistied Micro Patterning of Anodic Oxide Film of Aluminum”.

In May, Prof. Takahashi and Assoc. Prof. Sakairi attended the Aluminum Surface Science and Technology 2006 in France and presented “Micro-Technology on Aluminum by Anodizing, Laser Irradiation and AFM Probe Processing” and “Effect of Porous Type Anodic Oxide Film Thickness on Galvanic Corrosion of Aluminum Alloys”. They also attended the 3rd Korea-Japan Joint Seminar for Capacitors Energy System (Korea, 2006. 5), and gave lectures on “New Technologies on Aluminum Surface Using Laser Irradiation and AFM Probe Processing” and “Electrochemical noise analysis of galvanic corrosion of anodized aluminum”.

In August, Assoc Prof. Sakairi attened the 57th ISE meeting in Edinburgh U. K. to present two papers entitled "Effect Of Anodizing On Corrosion Of Al-Zn Alloy Coated Steels In Chloride Environments" and "Effect Of Temperature On Oxide Film Reformation Of Titanium In Vitro With Photon Rupture"

In November, the 10th Symposium of University of Science Technology Beijing & Hokkaido University was held in Beijing, and Prof. Takahahshi and Mr. Nagahara attended the symposium. They presented papers entitled “Fabrication of Three-Dimensional Micro-Manipulator by Laser Irradiation and Electrochemical Technique” and “Cathodic Pplarization of anodized Niobium Electrode in A Borate Solution”

Presentations

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Study On Corrosion Protection Of Anodized Aluminum, Y. Shimoyama, M. Sakairi and H. Takahashi, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, Jan., 2006.

Observation of Growth of Anodic Oxide Films on Aluminum by Scanning Confocal Laser Microscopy; R. Ohshima, N. Katayama, T. Kikuchi, and H. Takahashi: Joint meeting Hokkaido Secs. of Chem. Soc. Jpn. and Soc. Anal. Chem., Sapporo, Feb., 2006.

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Effect of Anodic Oxide Film Structure On Corrosion Resistance Of Coated Steels; Y. Uchida, M. Sakairi, and H. Takahashi: ibid.

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Effect of Anions on Localized Corrosion of Titanium in Vitro; M. Sakairi and H. Miyata: ibid.

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Measurements of Potential Distribution on Welded Stainless Steel with Small Drop Cell ; T. Nakayama, M. Sakairi, K. Fushimi, and S. Hashizume: Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, July, 2006.

Effect Of Anodizing On Corrosion Of Al-Zn Alloy Coated Steels In Chloride Environments, 57th ISE meeting, Edinburgh U. K., August, 2006.

Micro-patterning and Area Selective Metallization on Anodic Oxide Film of Aluminum by Laser Irradiation; H. Jha , T. Kikuchi, M. Sakairi, and H. Takahashi: The 59th Meeting of Colloid and Interface Chemistry, Sept., Sapporo, 2006

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Cathodic Polarization of Anodized Niobium Electrode in Borate Solution; K. Nagahara, M. Sakairi, H. Takahashi, and T. Izumi: ibid.

LABORATORY OF HIGH TEMPERATURE MATERIALS

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Research work at “Laboratory of high temperature materials” directs toward 1) high-temperature oxidation of metal silicides, 2) high-temperature oxidation of metal disilicides in H_2O-containing atmosphere, 3) microstructures of oxidation scales formed on NiAl-X alloys, 4) interface reactions between $NbSi_2$ or B-$NbSi_2$ and Nb 4) sintering and synthesis of silicide-based composites, 5) structures of oxide scales formed on steels and aluminum alloys in H_2O-containing atmospheres, and 6) corrosion behavior of iron-based alloys in molten lead-free solders.
Current topics on research are in the following:

(1) Oxidation behavior of metal silicides in air
In order to clarify the oxidation behavior of metal disilicides, high-temperature oxidation tests are being done. In particular, the requisite vapor pressure of metal oxide for the formation of a SiO_2 scale was clarified from the observation of the oxide scales formed on B added W, and Mo disilicides. Mechanisms of oxidation of various metal disilicides are also being clarified.

(2) Oxidation behavior of metal disilicides in H_2O-containing atmospheres

The Effect of Ni concentration on the steam-oxidation behavior of various Cr-Si-Ni compacts is being investigated. The results demonstrated that increasing Ni content led to gradual change from SiO_2 scale- to Cr_2O_3 scale-formation and consequently the addition of 20% Ni into $CrSi_2$ was the most effective for steam oxidation. Steam-oxidation behavior of B-added WSi_2 and $MoSi_2$ is also being investigated. The addition of B was appreciably effective for the improvement of oxidation and steam-oxidation.

(3) Microstructures of oxide scales formed on NiAl-X alloys

Microstructures of oxide scales formed on NiAl-X (=Zr, Cr) at 1323 K are being observed by TEM. Based on the results, mechanisms of spalling of an alumina scale formed on NiAl and suppression of spalling by addition of Zr and Cr were proposed.

(5) High-temperature oxidation of steels and aluminum alloys in H_2O-containing atmospheres

In order to clarify the effect of H_2O vapor on oxidation behavior of steels in a hot rolling process, oxidation tests of some carbon steels at 1473 K in $(N_2\text{-}3\%O_2)\text{-}XH_2O$ atmospheres are being done. The results showed that the position of spalling of oxide scale during cooling moved from the substrate/oxide scale interface to the $(Fe_3O_4+FeO)/FeO$ interface with increase in oxidation temperature, time, and carbon content in steels. Oxidation tests of aluminum alloys are also being carried out in air and H_2O-containing atmospheres. The results indicated that Mg-containing Al alloys formed a MgO or MgO/Al_2O_3 scale, and the others (Al alloys) formed a Al_2O_3 scale.

(6) Corrosion behavior of iron-based alloys in molten lead-free solders

In order to examine the reaction between iron-based alloys and molten lead-free solders, corrosion tests of iron-based alloys were carried out at

573-773 K for 24 hr in molten lead-free solders. Corrosion resistance of iron-based alloys against molten lead-free solders was appreciably affected by the carbon concentration and microstructure of the alloys substrate.

Other activities:

In March, Prof. Kurokawa was invited to the International Symposium on High Temperature Materials towards VHTR held in Busan, Korea and presented a paper entitled “Oxidation behavior of metal disilicides”. In May, Prof. Kurokawa and Dr. Yamauchi attended the International Workshop on Designing of Interfacial Structures in Advanced Materials and their Joints held in Osaka, and presented papers entitled “Oxidation Behavior of Mo-Si-B In-Situ Composites” and “Classification of Oxidation Behavior in Disilicides”. In December, Dr. Yamauchi attended MRS Fall Meeting 2006 held in Boston, U.S.A. and also presented a paper entitled “Structure and Oxidation Behavior of Mo-Si-B composites produced by MA-SPS processes”.

Presentations

Formation of Protective Scale on Silicides and Their Service Temperature; K. Kurokawa: The seminar of Jpn. Inst. Metals, Tokyo, Feb., 2006.

Effect of Zr Addition on Structure of NiAl and Al_2O_3 Interface; S. Kawata, K. Kurokawa, S. Watanabe, A. Yamauchi and T. Narita: The 13th Annual Meeting of Inst. of Applied Plasma Sci., Fukuoka, Mar., 2006.

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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 Temperature Furnace
Micro-Thermobalance

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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) and Protective Dentistry(Prof.Manabu Morita).

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 muti-wall CNTs(SWCNT, MWCNT) and CNF were used with the aim of the biomedical application and the pretreatment method of purification, solubilization, dispersion, surface modification were developed. Biochemical cell functional test of cell survival rate, LDH activity, emission of oxygen radicals and cytokines IL-1β, IL-8, TNF-α, M-CSF and implantation test in soft tissue was done and bioreaction was evaluated. With the decrease of particle size the cytotoxicity originated from the physical size effect was pronounced especially below 10μm. Maany interesting properties advantageous to buomedical 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 monotubes as delivery system of DNA, protein, saccharic tips and the sintered bulk as implant materials are also developed.

(2) Development of functionally graded dental implant

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

(3) Modifications of carbon nanotubes for biological applications

For biomedical applications of carbon nanotubes (CNTs), new modification methods to give bioactivity or biocompatibility are needed for achievement of various required designs. Modification and immobilization of various functional molecules on CNTs by covalent and non-covalent methods were investigated. Multi-walled carbon nanotubes (MWNTs) coated with a carbohydrate-carrying polymer can be easily prepared by a non-covalent and via hydrophobic interactions. The carbohydrate coated MWNT was found to acquire a selective binding affinity to the corresponding lectin without a nonspecific interaction. On the other hand, a bare MWNT interacted nonspecifically with lectins. These results showed that a MWNT coated with a carbohydrate-carrying polymer has the biological recognition signals. Secondly, we developed a biomimetic coating method to produce the architecture of crystalline apatite at nano-scale levels on the surface of MWNTs. After immersion of MWNTs in revised simulated body fluid (r-SBF), the crystallites at nano level were grown radially originating from a common center in the middle of a single MWNT and perpendicularly to the longitudinal direction of MWNT. MWNTs with the defined surface morphology of nano apatite crystallites could be useful as biomaterials for scaffolds and for the biomedical applications.

(4) Development of FRP esthetic orthodontic wire

To realize the esthetic, transparent orthodontic wire the FRP wires of the diameter 0.5mm with the multiple fiber structure has been fabricated by either drawing of fiber-polymer complex at 250C or photopolymerization method. Biocompatible CaO-P_2O_5-SiO_2-Al_2O_3 (CPSA) glass fibers of 8-20mm in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bis-GMA. The improvement has been done to obtain the adequate flexural strength and higher torque. FRP wire shows the sufficient flexural strength and a very good elastic recovery. The dependence of Young's modulus and flexural stress on fiber fraction obeys very well the rule of mixture. This FRP wire can cover the range of the strength corresponding to the conventional metal orthodontic wires from Ni-Ti used in the initial stage of orthodontic treatments to Co-Cr used in the last stage by changing the volume ratio of glass fibers with the same external diameter. FRP wire can satisfy both mechanical properties and estheticity, which is not possible for the conventional metal wire.

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

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

The animal experiments to implant various sizes of Ti particles of 1-100μm and macroscopic cylindrical Ti implant in mm order for 3 days to 8 months showed that the macroscopic size of Ti was encircled with fibrous connective tissue layer from early stage and there was no inflammation. As the size of particle becomes smaller, many phagocytic cells appear with fibrous connective tissue layer inside the particle inserted region and tissue showed inflammation. It takes more time to encircle the particle-contained tissue region and heal inflammation. For 1-3μm the inserted region is never encircled with fibrous connective tissue layer and inflammation continues.

The in vitro cell functional tests on cell 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, TNF-α, was not detected in any solution of Ni, V, Ti, the simulated body fluid(Hank's solution) mixed with 10mm paricles of Ti and with submicron size Ni particles. TNF-α was found only in the 1-3μm Ti particle mixed Hank's solution, which suggests that particles were phagocytized. SEM observation and EDS elemental analysis confirmed the phagocytosis of Ti particles by neutrophils.

The difference of cell reaction to 1-3μm and 10μm Ti particles suggests that the particles(1-3μm) smaller than cell size(about 5μm 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. Physical-mechanical anchoring effect plays an important part in binding force between teeth and composite resin. The pretreatment to make etching of teeth is generally done using acid agents for enhancement of binding. SEM is usually used for the evaluation of etching effect. It can observe, however, only the result after a certain etching time. To observe the sequence of etching process it is necessary to prepare the series of specimens treated with different etching time. Atomic force microscope is applied for the in-situ observation of etching process of human enamel and dentin in acid agents. The chronological change of surface morphology can be successively observed and quantitative analysis is done for different etching conditions.

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

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

(8) Radiation effects on polymer resin :

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

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

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

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

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

(11) Tissues and dental materials observation by XSAM

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

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

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

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

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

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

The current photocatalysis of anatase TiO_2 mostly works only by ultraviolet light. To make applicable for medical use it is necessary to develop the visible-light reactive photocatalysis. Visible light sesitization was obtained by surface modification with caions of Au, Ag, Cu, Pt, Pd. Depigmentation with visible light around 470nm which is used for photopolymerization of composite resin restoration in dental clinics could be done with the Ag activated TiO_2 in contrast to very little effect in an untreated TiO_2. Antibacterial effect was also confirmed to streptococcus mutans, one of the most popular bacteria for caries. The application to bleaching of pigmented teeth was developed.

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

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

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

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

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

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

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

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

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

Other activities:

The three-year research project in nanomedicine under the subject of "Development of Visualization Method of Internal Motion of Nanoparticles (H18-Chem-General-006)" started for the three year as Research on Advanced Medical Technology under Health and Laybour Sciences Research Grants from the Ministry of Health, Laybour and Welfare of Japan. The project team is constitute of Leader: Prof.Fumio WATARI, Assigned Researchers: Prof.Yasunori TOTSUKA, Prof. Yoshimasa KITAGAWA, Prof. Manabu MORITA, Prof. Atsuro YOKOYAMA (Graduate School of Dental Medicine, Hokkaido University), Prof. Kiyotaka ASAKURA, Prof. Somei OHNUKI, Prof. Bunshi FUGETSU, Assoc.Prof. Haruichi TOYAMA (Hokkaido University), Prof.Kazuyuki TOHJI(Tohoku University), Prof. Kenzo ASAOKA (Tokushima University), Prof. Kunio ISHIKAWA (Kyushu University), Masayuki OKAZAKI(Hiroshima University) and other Collaborating Researchers.

Dr.SUSAN Liao of Tsinghua University, Beijing, China finished the cooperative study as the postdoctoral researcher of the Japan Society for Promotion of Science (JSPS) for the development of nanohydroxyapatite-collagen composite as bone substitute biomaterials.

The international collaborations are continued with Institute of Dental Materials Science, Umea University, SWEDEN (Emerita Prof. Maud BERGMAN) on application of Ti, ZrO_2, amalgum for dentistry, and research on side effects, with Department of Dental Materials, Chonbuk National University, KOREA (Prof.Tae-Sung BAE) on evaluation of mechanical properties of laser-welded Ti, dental porcelain, with Institute for Materials Science, Dresden Institute of Technology, GERMANY (Prof.W.POMPE) on the biocompatibility evaluation and application of collagen-hydroxyapatite composites and with Biomaterials Laboratory, Department of Materials Science and Engineering, Tsinghua University, CHINA (Prof.FZ CUI) on the development and biomedical application of nanobiomaterials, University Polytechnica Bucharest, Bucharest, Romania (Dr. ROSCA Iosif Daniel) on the development of polymer biomaterials.

The collaboration with Laboratory for Advanced Materials, Institute for Materials Research, Tohoku University (Assoc.Prof.Mamoru OMORI) is undergoing on the fabrication of new biomaterials including bulk carbon nanotubes and functionally graded materials by applying a spark plasma system(SPS) as a method to enhance sintering. The development of FRP esthetic orthodontic wire has continuously been done with Department of Industrial Chemistry, Chiba Institute of Technology(Associate Prof.Masahiro KOBAYASHI).

Presentations

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Tissue reaction for the materials depend on their size –micro/nano size effect-, F. Watari, The 114th General Session of the Society for Surface Engineering, Sapporo, Oct. 2006.

Tissue reaction for micro/nano particles, F. Watari, K. Tamura, The 28th General Session of the Japanese Society for Biomaterials, Tokyo, Nov. 2006.

Distribution and chemical state analysis of rarely contained metallic elements in biological tissues, M.Uo, K.Akasaka, F.Watari, A.Yokoyama, T.Kohgo, Y.Totsuka, Asian Bioceramics Congress 2006, Bangkok, Nov.

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Response of osteoblastic cells grown on carbon nanotubes scaffold, N. AOKI, A. YOKOYAMA, Y. NODASAKA, T. AKASAKA, M. UO, Y. SATO, K. TOHJI, F. WATARI, 31st Fullerene-Nanotubes General Symposium, Tsu, 107,2006

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Biomedical properties of surface carbonized titanium, YH.Zhu, M.Shimozuma, M.Uo, W.Wang, F.Watari , The 47th General Session of the Japanese Society for Dental Materials and Devices. Tokyo, Apr, 2006.

Facilities and Capabilities

XSAM: HORIBA XGT-2000V, Scanning X-ray analytical microscope for elemental mapping analysis
XRD: Rigaku Multiflwx, X-ray diffractometer (3kVA)
AFM : TopoMetrix TMX2000 Explorer, AFM for dry and wet specimens
NSOM : TopoMetrix Aurora, Near field Scanning Optical Microscope
Laser Raman Spectrometer : Dilor Labram, Laser Raman Spectrometer with mapping analysis
ICP : HITACHI P-4010, ICP emission spectrometer for analysis of elements in aquaous solution
FT/IR : Jasco FT/IR-300E, FT/IR spectrometer with microscopic IR measurement
Particle Size Analyzer : Shimadzu SALD-7000, Particle size distribution analysis with laser scattering
Surface Area Analyzer : Shumadzu, Surface area analysis with gas absorption/desorption
Universal Testing Machine : INSTRON MODEL 4204, Testing for mechanical properties of materials
Laser Welder : ATJ TLL7000, Nd-YAG pulse laser welder with computer controlled x-y stage
Cold Isostatic Press : Hiikari Koatsu Kiki (10000atm type and 20000atm type)
:Kobelco, Large volume isostatic press (4000atm)
Vickers Hardness Tester: Shimadzu
Acoustic Emission : Physical Acoustic Corporation
Thermal Gravitometry and Differential Thermal Analysis(TG/DTA) : Rigaku

Denki
Diamond Cutter : Buehler and Struers diamond cutter

LABORATORY OF ADVANCED HIGH-TEMPEARTUER MATERIALS

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The research activities of the laboratory are directed to a study and development of the advanced high strengthened ODS alloy system and high temperature corrosion, oxidation and protection of metals.

Presentations

Effects of Hf on oxidation behavior of the Ni-22Al-30Pt Alloy; S. Hayashi, T. Narita, and B. Gleeson : Jpn, Inst. Metals, March 2006.

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Microstructural development of Re-based diffusion barrier coating during a formation; E. Wang, T. Suda, S. Hayashi, S. Ohnuki, and T. Narita : Jpn, Inst. Metals, March 2006.

Short-term oxidation behavior of oxidation resistant coating formed on TiAl alloy; T. Nishimoto, S. Hayashi, and T. Narita : Jpn, Inst. Metals, March 2006.

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The oxidation behavior of FeCrAl-(0-0.Ti) at 900°CX: Y. Kitajima, S. Hayashi, T. Narita, and S. Ukai : ISIJ and Jpn, Inst. Metals joint meeting, July. 2006.

The oxidation behavior of FeCrAl-X (X=Re, Ta, Mo, Mn, Nb, Cu, Co, W, Ti) alloys: Y. Kitajima, S. Hayashi, T. Narita, and S. Ukai : Jpn, Inst. Metals, March 2006.

Phase constitution of (Ni-10Al)-10Re alloy at 1473K; K. Kato, S. Hayashi, T. Narita, T. Takashima, and S. Saito : Jpn, Inst. Metals, Sep. 2006.

Diffusion behavior of each element in Re-Cr-Ni system at 1573K; S. Saito, T. Takashima, S. Hayashi, and T. Narita : Jpn, Inst. Metals, Sep. 2006.

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Interdiffusion and oxidation of Platinum coated TMS82+, NiCrAl and NiCrCoAl alloys, S. Ford, S. Hayashi, and T. Narita, 53rd Japan Conference on Mat. and Env., Sep. 2006.

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Development of Super ODS for Next Generation (2) Mechanical Alloying, N. Iwata, L. Tong, R. Kasada, A. Kimura, S. Ukai, T. Okuda: Atomic Energy Society of Japan, Fall Meeting, September 27-29, 2006

Development of Super ODS for Next Generation (3) Tensile Properties, R. Kasada, A. Kimura, S. Ukai, T. Okuda, F. Abe, S. Ohnuki, T. Fujisawa, T. Kobayashi: Atomic Energy Society of Japan, Fall Meeting, September 27-29, 2006

Development of Super ODS for Next Generation (4)Corrosion Properties by Super Critical Water, T. Sou, A. Kimura, S. Ukai, T. Okuda, F. Abe, S. Ohnuki, T. Fujisawa, T. Kobayashi: Atomic Energy Society of Japan, Fall Meeting, September 27-29, 2006

Development of Super ODS for Next Generation (5) Ion Irradiation Test, H.Kishimoto, R. Kasada, A. Kimura, S. Ukai, T. Okuda, F. Abe, S. Ohnuki, T. Fujisawa, T. Kobayashi: Atomic Energy Society of Japan, Fall Meeting, September 27-29, 2006

LABORATORY OF SPECIALLY PROMOTED RESEARCH

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The research activities of the laboratory of Specially Promoted Research, (2006~2010), supported by Japanese Government, are directed to elucidating of the interaction between alloys (super alloys, Ni-based alloys and Fe-based alloys), coatings and corrosive gas atmospheres at high temperature, to understanding of the influence of coatings on mechanical properties and to development of a new bond-coat with diffusion barrier to realize high reliability and long life. Furthermore, we aim at practical use by technology transfer to gas turbines and jet engines.

Current topics on research are in the following:

(1) Formation of oxidation resistant coating with diffusion barrier

A new bond-coat with a duplex layer structure, an inner σ-(Re, Cr, Ni) as a diffusion barrier and an outer Ni-aluminide as Al reservoir, was formed on

Ni-based superalloy and on Hastellloy X. Diffusion barrier layer was produced by Re-Ni and Ni-W electroplating from aqueous solutions followed by Cr pack cementation at high temperature. Al reservoir layer was formed by Ni electroplating, followed by Al pack cementation.

(2) Oxidation behavior of oxidation resistant coating with diffusion barrier

Oxidation behavior of oxidation resistant coating with diffusion barrier on Ni-based superalloy and Hastellloy X was investigated. Oxidation tests were carried out at temperature between 1323 and 1423K in air. It was found that σ-(Re, Cr, Ni) act as a diffusion barrier for both inward diffusion of Al and outward diffusion of alloying elements in the alloy substrate.

(3) Interdiffusion of Platinum coated superalloy and model alloys

Interdiffusion of Pt in superalloy and model alloys with nominal composition Ni-6Cr-12Al and Ni-6Cr-8Co-12Cr (at.%) was investigated. Pt was electroplated on these alloys to a thickness of 5 μm. These samples were then heat-treated at 1273K for 1, 10, 50 and 100hrs in vacuum. Specimens were cross-sectioned and prepared for analysis using an argon ion cross-polisher (CP), and then imaged by SEM or FIB. Cross-sections were chemically analyzed EPMA.

(4) Effect of titanium on the suppression of meta-stable alumina formation

The effect of titanium on the suppression of meta-stable alumina formation on alumina-former alloys (Ni-Al and Ti-Al) was investigated. To suppress the fast growth of meta-stable alumina phases at 1073～1173K, a thin layer of titanium was deposited on the NiAl alloy by a vacuum evaporation method. Surface morphological observation and XRD showed that uncoated NiAl alloy formed needle-like gamma or theta alumina at 1173K, however, no whiskers were observed on the surface of Ti coated NiAl.

Presentations

Early-stage oxidation behavior of oxidation resistant coatings on TiAl alloy; T.

Nishimoto, S. Hayashi, and T. Narita: JPN, Inst. Metals, Tokyo, Japan, March 2006

Diffusion and oxidation of Pt plated NiCrAl alloys and TMS82$^+$ superalloy; S. Ford, S. Hayashi, and T. Narita: JPN, Inst. Metals, Tokyo, Japan, March 2006

Oxidation behavior of the coatings with a fine, multi-phase structure on TiAl alloy at high temperature: T. Nishimoto, S. Hayashi, and T. Narita: 3rd International Workshop on gamma TiAl Technologies, Frankfurt Germany, May 2006

Effect of coatings on the mechanical property and oxidation behavior of TiAl alloys at 1173K in air: T. Narita, S. Hayashi and T. Nishimoto: 3rd International Workshop on gamma TiAl Technologies, Frankfurt Germany, May 2006.

Investigation of structure and element distribution in alpha-alumina on TiAl alloys; T. Nishimoto, S. Hayashi and T. Narita: JPN, Inst. Metals, Niigata, Japan, September 2006

Investigation of early-stage oxidation behavior of oxidation resistant coating on TiAl alloy; T. Nishimoto, S. Hayashi and T. Narita: Proceedings of the 53rd Japan Conference on Materials and Environments, Akita, Japan, September 2006

Interdiffusion and oxidation of platinum coated TMS82$^+$, NiCrAl and NiCrCoAl alloys: S. Ford, S. Hayashi and T. Narita: The 53rd Japan Conference on Materials and Environments, Akita, Japan, September 2006

Effect of W on Mo enrichment into diffusion barrier coating; T. Yoshioka, T. Nishimoto and T. Narita: Proceedings of the 53rd Japan Conference on Materials and Environments, Akita, Japan, September 2006

Effect of external tensile stress on oxidation behavior of nickel based alloy with Re-based diffusion coating, EFC-Workshop, Frankfurt, Germany, October 2006

Thermal Barrier Coating - Roles of Bond Coat and Diffusion Barrier-: T. Narita, T. Yoshioka, T. Nishimoto, and S. Hayashi; The 2nd Tsukuba International Symposium on Advanced Coatings in NIMS, Tsukuba, Japan November 2006

AFFILIATE MEMBERS

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Member of the committee for the study of *SABI* [rust] chemistry, Japan Society of Corrosion Engineering, and also of the organizing committee of the Ion Exchange Society. Research interests in the role of rusts in corrosion of iron and steel, as well as in the preparation and characterization of layered metal oxides and metal oxides in general as corrosion products from metals and as inorganic fine materials.

Presentations

Effect of Rusts on Corrosion of Steels; H. Tamura: 2006 Joint Meeting of 3 Society Sections, Sapporo, Feb., 2006.

Steel Protective Properties of Rusts; H. Tamura: 73rd Annual Meeting of Electrochem. Soc., Hachioji, Apr., 2006.

Application of the Frumkin Isotherm to Ion-Exchange Equilibria; H. Tamura: 6th International Symposium on Surface Heterogeneity Effects in Adsorption and Catalysis on Solid, Zakopane, Poland, Aug., 2006.

A Mechanism of Formation and Development of Rusts and Corrosion Protective Properties: H. Tamura: 53rd Japan Conference on Materials and Environments, Akita, Sept. 2006.

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Our group has intended to explore the fundamental corrosion mechanism of metals, development of corrosion monitoring system, surface finishing of aluminum and magnesium alloys, and numerical simulation of adatom on electrode.

Students

Kei Iokibe, Takeshi Sakamoto, Elsentriecy Hassan Hamed, Atsushi Naganuma, Miho Nakajima, Shinnosuke Egoshi, Toshiro Nakamura, Humiyasu Nishiyama, Yosuke Fujieda

Presentations

Effect of Sulfuric Acid containing Cu ions on Zincate Pretreatment of Al-Si Alloy, S. Egoshi, K. Azumi, M. Seo, S. Kawashima and Y. Koyama; The Joint Meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Jan., 2006.

Corrosion of Cu embedded in Bentonite Clay, M. Nakajima, K. Azumi and M. Seo; *ibid*.
Development of Tungsten pH Sensor Usable in Thin Electrolyte Solution, T. Nakamura, K. Fushimi, K. Azumi, and M. Seo; *ibid.*

Measurement of Corroding Copper in Underground Environment using Resistometry, M. Nakajima, K. Azumi and M. Seo; The 113th Annual Meeting of Surf. Finish. Soc. Jpn., Kawagoe, Mar., 2006.

Effect of Cu pretreatment on Zincate Process of Al-Si alloy, S. Egoshi, K. Azumi, M. Seo, S. Kawashima and Y. Koyama; *ibid*.

Improvement of Corrosion Resistance of AZ91D Magnesium Alloy by Stannate Chemical Conversion Coatings, El Sentriecy Hassan, K. Azumi and H. Konno, The 114th Annual Meeting of Surf. Finish. Soc. Jpn., Sapporo, Oct., 2006.

Development of Multichannel Electrode System and Its Application to Crevice Corrosion, A. Naganuma, K. Fushimi, K. Azumi, H. Habazaki; *ibid*.

ab-initio MO Calculation of Zn cluster, K. Iokibe, H. Tachikawa, K. Azumi; *ibid*.

Model Experiment of Edge Corrosion of Coated Steel Sheets using Multiple Electrodes System, K. Azumi and K. Iokibe; The 152th Fall Meeting of Iron and Steel Insts. Jpn., Niigata, Sept., 2006.

Effect of Minute Amount of Cu Deposition on Zincate Substitution Reaction of Al Alloys, Shinnosuke Egoshi and Kazuhisa Azumi; ISE Meeting, Edinburgh, Sept. 2006.

Density Functional MO Calculation for Zn Cluster, K. Iokibe, H. Tachikawa, K. Azumi; *ibid*.

Current Transients from Type-185N Stainless Steel Observed during Micro-indentation Test in pH 8.4 Borate Buffer Solution, T. Yamamoto, K. Fushimi, K. Azumi and M. Seo; *ibid*.

A Numerical Model of Rupture and Repair of Passive Film on Iron in pH 8.4 Borate Buffer during Micro-indentation; K. Fushimi, T. Yamamoto, K. Azumi and M. Seo; *ibid*.

Application of segmentized electrode system to corrosion monitoring, K. Azumi, K. Fushimi and A. Naganuma; *ibid*.

ABSTRACTS of PUBLICATIONS

Reduction of SiO_2 to Si by Aluminum Metal Fog in NaCl-KCl-$AlCl_3$ Molten Salt

Mikito Ueda, Yoshihisa Abe, and Toshiaki Ohtsuka

Materials letters, **60**, 635-638 (2006)

Direct reduction from SiO_2 to metallic Si by aluminum metal fog was attempted in NaCl-KCl molten salt. The aluminum metal fog was evolved by contact of liquid aluminum metal to Al(III) in the molten salt. The metal fog forms in the molten salt an atmosphere enough reductive to induce a reaction from SiO_2 to Si. The immersion of SiO_2 plate at the aluminum metal fog in the molten salt caused the color change of the plate, and the plate exhibited the darker color with time. From EPMA and XRD analysis, metallic crystallized Si was detected in the darkened area. From the color change with time, the reaction proceeding was discussed.

Local deposition of polypyrrole on aluminum by anodizing, laser irradiation, and electrolytic polymerization and its application to the fabrication of micro-actuators

Y. Akiyama, T. Kikuchi, M.Ueda, M. Iida, M. Sakairi, H. Takahashi

Electrochimica Acta, **51**, 4834-4840 (2006)

Polypyrrole was deposited at selected areas on aluminum by anodizing, laser irradiation, and electrolytic polymerization, and the application of the technique for fabricating micro-actuators was attempted. Aluminum specimens covered with porous type anodic oxide films were irradiated with a pulsed Nd-YAG laser to remove the oxide films locally, and then thin Ni layers were deposited at areas where film had been removed. Polypyrrole could be successfully deposited only on the Ni layer by anodic polarization of the specimens in pyrrole monomer solution, and a polypyrrole/Ni bilayer structure could be obtained by dissolution of the aluminum substrate and anodic oxide film in NaOH solutions. The bilayer structure was found to be inactive to doping and dedoping of ions during anodic and cathodic polarization. A three-layer structure, nitrocellulose/Ni/polypyrrole, fabricated by electrolytic polymerization after nitrocellulose coating on a Ni layer detached from the aluminum substrate, showed ion-doping and-dedoping activity, suggesting the possibility of fabricating micro-actuators in this manner.

Structural and electromagnetic characterization of Fe-SrF_2 granular films

H. Hosoya, M. Arita, K. Hamada, Y. Takahashi, K. Higashi, K. Oda and M. Ueda

J.Phys. D: Appl. Phys. **39**, 5103-5108 (2006)

We investigate composite Fe-SrF_2 films to explore new materials showing the granular-type tunneling magnetoresistance(TMR)effect. The films are composed of Fe nano-particles embedded in a SrF_2 matrix. The electromagnetic properties of the ferromagnetic metal-insulator films are confirmed, including super-paramagnetism, tunnel conduction and TMR. We obtain a TMR of 3% at RT and 5% at 77K. The films resistivity is much higher than that of oxide-based granular film. We also fabricate the nanostructures of granular films and aim at the application of the single-electron transistor. As a result, we observed a Coulomb blockade.

Polypyrrole coating doped by molybdo-phosphate anions for corrosion prevention of carbon steels

Toshiaki Ohtsuka, Masahide Iida, and Mikito Ueda

J. Solid State Electrochemistry, **10**, 714 (2006)

The polypynole coating was prepared from phosphoric acid aqueous solution containing the hetero-polyanion $PMo_{12}O_{40}^{3-}$ and pyrrole monomer to make new coating for corrosion prevention of carbon steels. The coating thus formed in the phosphate acid solution was doped by $PMo_{12}O_{40}^{3-}$ and by PO_4^{3-}. The coating was flexible enough to cover the steel homogeneously without cracks, although many cracks were observed on the coating formed in a neutral aqueous solution of Na_2MoO_2. The 5.1-μm-thick polypyrrole coating makes the steel maintain the passive state for 48 h in neutral 3.5wt% NaCl solution at pH5,3 and for 80h in acidic 3.5wt% NaCl solution at pH 1.9. The coating decreased the corrosion rate of the steel by 1/200 in the neutral NaCl solution and by 1/340 in the acidic NaCl solution, if compared with the rate of the bare steel. The dissolution current of the steel during the immersion at the level of the typical passive current in the respective solutions.

Quantative determination of corrosion products and adsorbed water on copper in humid air containing SO_2 by IR-RAD measurements

Takeshi Sasaki, Jun Itoh, Yuuki Hiriguchi, and Toshiaki Ohtsuka

Corr. Sci., **48**, 4339-4351 (2006)

The time dependency of the amounts of corrosion products and co-existing adsorbed water on copper in humid air containing SO_2 was estimated from a series of in situ time-resolved IR-RAS spectra on the basis of the relations between the band intensities and the mass changes of the corrosion products, which were determined by simultaneous measurement of IR-RAs and QCM. The amounts of both corrosion products increased slowly at the initial stage and later increased rapidly. Although the relative humidity was kept constant, the amount of adsorbed water increased nearly the same behavior as that of corrosion products in the stage of relatively small amounts of corrosion products and later increased rapidly when the amounts of corrosion products increased. In humid air without SO_2, sulfite gradually decomposed and some of it changed into sulfate.

Passivation Oxide Films and Rust Layers on Iron

T. Ohtsuka

Characterization of Corrosion Products on Steel Surfaces, Y. Waseda and S. Suzuki (Editors), Springer, (2006) pp. 19-31.

The thermodynamic and kinetics were reviewed on the passive oxide film and rust on iron. The ionic migration through the passive oxide film is followed by a model proposed by Cabrara and Mott, in which the thickness of the oxide film was determined by an ionic migration current assisted by the high electric field in the film and by a dissolution current of iron ions from the film to electrolyte. The composition was surveyed by in-situ various methods as well as ex-situ methods and was not made clear in the present. Most probable composition has been assumed to be g-Fe2O3; however, it may be disordered. The iron rust can be formed on the passive film by an anodic deposition from Fe(II) ions in electrolyte to hydrated Fe(III) oxyhydroxide.

Spark anodizing of titanium for biomedical applications

E. Matykina, M. Montuori, J. Gough, F. Monfort, A. Berkani,
P. Skeldon, G.E. Thompson and H. Habazaki

Trans. Inst. Met. Finish., **84**, 125-133 (2006).

Spark anodising of titanium enables fabrication of coatings with potential biocompatibility. In the present study, coatings were produced in electrolytes containing various amounts of $CaHPO_4$, $Ca(H_2PO_4)_2$, $Na_6P_6O_{18}$ and $Ca(CH_3COO)_2$. The findings disclose formation of coatings with compositions, morphologies and structures dependent upon the growth conditions. Calcium and phosphorus species are distributed throughout most of the coating thickness, with typical Ca/P atomic ratios of similar to 0.45 and (Ca+P)/Ti atomic ratios in the range 1.0-2.6 in the near surface regions. Calcium contents in particular reduced towards the metal. Dissolution behaviour in physiological solution was investigated by potentiodynamic polarisation measurements and immersion tests, the latter indicating titanium loss rates of similar to 0.3 μg cm^{-2} day^{-1}. Preliminary adhesion studies using primary human osteoblast cells revealed favourable cell responses to the anodic coatings. Further, the deposition of hydroxyapatite by cathodic deposition in selected electrolytes indicates scope for additional tailoring of coating surfaces. More limited studies of Ti-6Al-4V alloy demonstrated coating formation broadly similar to that on titanium, but with incorporation of aluminium and vanadium species and increased loss rates of titanium, similar to 4 μg cm^{-2} day^{-1}, in immersion tests.

A flow model of porous anodic film growth on aluminium

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

Electrochim. Acta, **52**, 681-687 (2006).

The development of pores in a classical porous anodic film formed on aluminium in phosphoric acid solution is investigated. The study employs a tungsten tracer layer that is incorporated into the anodic film from the aluminium substrate, followed by detection of the tracer by transmission electron microscopy and Rutherford backscattering spectroscopy. Distortions of the tungsten layer on entry into the film and retention of tungsten species in the film are compatible with porosity arising mainly from flow of anodic oxide beneath the pore bases towards the cell walls. The behaviour is contrary to expectations of a dissolution model of pore formation.

High rate capability of carbon nanofilaments with platelet structure as anode materials for lithium ion batteries

H. Habazaki, M. Kiriu and H. Konno

Electrochemistry Communications, **8**, 1275-1279 (2006).

Carbon nanofilaments (CNFs) with platelet structure have been prepared by liquid phase carbonization using porous anodic alumina template, and their lithium ion insertion/extraction properties have been examined as a function of heat treatment temperature and filament diameter. The CNFs heat-treated at 1000 °C reveal higher capacitance and higher rate capability compared with those heat-treated at higher temperatures. Further, it is found that higher reversible capacity is obtained for the CNFs with reduced diameter. The reversible capacity of highly graphitized CNFs formed at 2800 °C is less than 200 mA h g^{-1} at a current density of 50 mA g^{-1}, being far lower than the theoretical capacity (372 mA h g^{-1}) of graphite. A probable reason is the presence of loop at the edge of graphene layers.

Suppression of Field Crystallization of Anodic Niobia by Oxygen

H. Habazaki, T. Ogasawara, H. Konno, K. Shimizu, S. Nagata, K. Asami, K. Takayama,
P. Skeldon and G.E. Thompson

J. Electrochem. Soc., **153**, B173-B177 (2006).

Solid-solution Nb-O films containing up to 50 atom % oxygen, prepared by magnetron sputtering, were used to investigate the influence of the oxygen on field crystallization during anodizing at 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K. The findings reveal that field crystallization is hindered dramatically by addition of 20 atom % oxygen to the substrate, while no crystallization occurs for a Nb-50 atom % O substrate. Prior thermal treatment accelerates field crystallization of niobium, but not the Nb-50 atom % O substrate. The thermal treatment is considered to promote generation of precursor sites for crystal nucleation. However, sufficient oxygen in the substrate may restrict precursor development and/or reduce the compressive stresses in the amorphous anodic niobia that can facilitate crystal growth.

Synthesis of single- and multi-component carbides utilizing exfoliated graphite

H. Konno, D. Abe and H. Habazaki

Tanso, **221**, 8-13 (2006).

Different metal alkoxides were impregnated into exfoliated graphite (EG) by sorption and hydrolyzed with steam. Thus formed precursors were pyrolyzed at 1500-1700ºC for 1-10 h in argon to form single- and multi-component carbides, such as ZrC, TiC, (Ti, Zr) C solid solns., TiC-ZrC composites, and TiC-Fe composites. In this process, hydrolyzed metal alkoxides were converted mainly to oxides and/or oxyhydroxides on the surface of graphite sheet composing EG, and eventually they are reduced to carbide or metal by graphite carbon at elevated temps. The small reaction spaces in EG produce fine metal carbide particles only by the pyrolysis. The process is simple and low cost, and possible to be developed to synthesize other carbides and composites.

Anodic behaviour of a model second phase: Al-20at.%Mg-20at.%Cu

Y. Liu, M.A. Arenas, P. Skeldon, G.E. Thompson, P. Bailey, T.C.Q. Noakes,
H. Habazaki and K. Shimizu

Corros. Sci., **48**, 1225-1248 (2006).

The anodic behaviour of sputtering-deposited Al-20at.%Mg-20at.%Cu alloy is investigated during anodizing and potentiodynamic polarization treatments using transmission electron microscopy, X-ray photoelectron spectroscopy and medium energy ion scattering. The composition of the alloy is close to that of the S-phase in 2024 aluminium alloy. The anodizing behaviour in both 0.1 M ammonium pentaborate and 0.1 M sodium hydroxide electrolytes follows the behaviour of more dilute, solid-solution, aluminium alloys, with enrichment of copper developing in the alloy during the growth of an alumina-based initial oxide containing incorporated magnesium species. Oxygen gas is generated following sufficient enrichment of copper for its oxidation to proceed and hence, for copper species to enter the oxide film. The generation of oxygen gas causes extensive damage to the film, which limits the voltage to relatively low values. Potentiodynamic polarization in 0.1 M sodium hydroxide electrolyte revealed mainly passive behaviour following an initial period of corrosion during which the passive film is developed. In this initial period, copper enriches in the alloy, beneath an oxide film containing aluminium and magnesium species. The magnesium species migrate faster through the film than the aluminium species and form a surface layer of $MgO/Mg(OH)_2$, which protects against losses of aluminium species to solution and permits the establishment of the passive film. The steady open-circuit potential of the passivated alloy in the hydroxide solution is about -550 mV (SCE), compared with about -1940 mV (SCE) for aluminium.

Generation of copper nanoparticles during alkaline etching of an Al-30 at.%Cu alloy

Y. Liu, M.A. Arenas, P. Skeldon, G.E. Thompson, H. Habazaki, K. Shimizu,
P. Bailey and T.C.Q. Noakes

Corros. Sci., **48**, 1874-1884 (2006).

A mechanism of formation of copper nanoparticles is proposed for alkaline etching of a sputtering-deposited Al–30 at.%Cu alloy, simulating the equilibrium θ phase of 2000 series aluminium alloys. Their formation involves enrichment of copper in the alloy beneath a thin alumina film, clustering of copper atoms, and occlusion of the clusters, due to growth of alumina around the clusters, to form nanoparticles. The proposed mechanism is supported by medium energy ion scattering, Rutherford backscattering spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy of the alloy following immersion in the sodium hydroxide solution, which disclose the enrichment of copper and the generation of the nanoparticles in the etching product of hydrated alumina. The generation of the nanoparticles is dependent upon the enrichment of copper in the alloy in a layer of a few nanometres thickness, with no requirement for bulk de-alloying of the alloy.

Anodic oxidation of InAlAs

A. Suleiman, Y. Liu, T. Hashimoto, P. Skeldon, G.E. Thompson, M.J. Graham, T. Quance,
H. Habazaki, K. Shimizu, P. Bailey and T.C.Q. Noakes

Corros. Sci., **48**, 126-136 (2006).

The anodic oxidation of InAlAs is investigated by transmission electron microscopy, Rutherford backscattering spectroscopy and medium energy ion scattering in order to elucidate the mechanism of oxide growth. For this purpose, anodizing was carried out at 5 mA cm^{-2} in 0.1 M sodium tungstate and 0.1 M ammonium pentaborate electrolytes at 293 K, which results in relatively efficient film growth over an initial voltage increment of about 70 V. In this period, an amorphous oxide develops with a formation ratio of 2.0 ± 0.2 nm V^{-1}. The film consists mainly of an outer layer of In_2O_3 and an inner layer of units of In_2O_3, Al_2O_3 and As_2O_3, the former representing about 14% of the film. There is suggestion of a fine, intermediate layer containing units of In_2O_3 and Al_2O_3 only. The layering correlates with the bond energies of the cation and oxygen species in the oxide and hence their relative migration rates. Further, for films formed in tungstate electrolyte, tungsten species are incorporated into the outer 40% of the film. Bubbles of oxygen gas are present in the film, probably developed within the In_2O_3 layer. At higher voltages, the film undergoes breakdown, with resulting major changes in the film morphology.

Effect of tetragonal ZrO_2 on the catalytic activity of Ni/ZrO_2 catalyst prepared from amorphous Ni-Zr alloys

M. Yamasaki, H. Habazaki, K. Asami, K. Izumiya and K. Hashimoto

Catalysis Communications, **7**: 24-28 (2006).

In zirconia-supported nickel catalysts, the influence of the ZrO_2 phase on the catalytic activity for CO_2 methanation has been investigated by TPD and TPR measurements. Ni/ZrO_2 catalysts with various amounts of the tetragonal ZrO_2 polymorph were prepared from amorphous Ni-Zr alloys by an oxidation-reduction treatment. The fraction of tetragonal ZrO_2 in the Ni/ZrO_2 catalysts increased with increasing nickel content of the amorphous alloy precursors. The methanation activity of Ni/ZrO_2 was strongly influenced by the ZrO_2 phase change. The tetragonal zirconia-supported nickel catalysts showed a higher turnover frequency for the methanation reaction and a greater CO2 adsorption than the monoclinic zirconia-supported nickel catalysts.

Preparation of mesoporous carbons by carbonization of the mixtures of poly（vinyl alcohol） with magnesium salts

T. Morishita, R. Suzuki, T. Tsumura, H. Habazaki, M. Inagaki

Tanso, **223**, 220-226 (2006).

Porous carbons with high surface area were successfully prepared from thermoplastic precursors, such as poly (vinyl alcohol) (PVA), by the carbonization of mixtures with MgO precursor at 900ºC in inert atmosphere. MgO in the carbonization products was dissolved out by using a diluted acid, either sulfuric or acetic acid. The carbon precursors with MgO precursors (reagent grade magnesium acetate and citrate) were mixed either in powder (powder mixing) or in aqueous solution (solution mixing). Pore structure of the resultant carbons depended strongly on the mixing method. The BET surface area of the carbons obtained through solution mixing could reach to very high value, such as 2000 m^2/g, even though any activation process was not applied. The carbons prepared through solution mixing method were rich in mesopores. By changing the size of MgO particles formed by pyrolysis of MgO precursor, the size of mosopores could be controlled. It was experimentally shown that substrate MgO was easily recycled.

Current Transients of Passive Iron Observed during Micro-indentation in pH 8.4 Borate Buffer Solution

K. Fushimi, K. Takase, K. Azumi, and M. Seo

Electrochim. Acta, **51**, 1255-1263 (2006).

Micro-indentation test of passive iron electrode in deaerated pH 8.4 borate buffer solution was carried out to investigate the rupture and repair of passive film. During driving a conical diamond micro-indenter with a load of 0.1 N order downward to the electrode and driving upward from the electrode, a couple of anodic current peaks were observed. The first current peak spiked during loading was responsible for partial exposure of iron substrate to the solution due to rupture of the passive film when the indenter tip contacted. The second peak emerged during unloading when elastic deformation recovered, which was ascribed to repair at the ruptured sites. The second peak current was larger than the first one. Both peaks were sensitively influenced by electrode potential or concentration of sulfate ions containing in solution. The model for a series of rupture and repair processes of the passive film by micro-indentation was proposed to discuss the current transients.

Fabrication of Micro-disk Electrode Probe by Electroless Nickel Plating

K. Fushimi, A. Naganuma, K. Azumi, and M. Seo

J. Surf. Fin. Soc. Jpn., **57(8)**, 592-596 (2006).

Fabrication of the micro-disk electrode probe, which is convenient for micro-electrochemistry of localized surface or in small amount of solution, has needed special equipments or technical skills. In order to fabricate a micro-disk electrode probe simply, nickel electroless plating in a glass pipette was applied. After activation of inside of a glass pipette heated and pulled off, nickel electroless-plating solution was successively introduced to deposit nickel in the pipette. Polishing tip of the pipette and/or electroplating Ni or Cu, Pt obtained a disk surface with a diameter less than a few ten micrometers. Cyclic voltammetry of the disk electrode showed a sigmoid curve and gave a limiting current which was identical with a theoretical value as a micro-disk electrode, indicating that this method was promising to fabricate the micro-disk electrode. The electroless-plating micro-disk electrode was employed as a probe of scanning electrochemical microscopy to demonstrate its performance. (Japanese)

Origin of Hydrogen in Anodized Niobium

H. Habazaki, K. Fushimi, H. Konno, K. Shimizu, K. Asami, P. Skeldon, and G.E. Thompson

J. Surf. Fin. Soc. Jpn., **57**(9), 676-678 (2006).

From GDOES depth profiling analysis of two different sputter-deposited niobium films anodized to 100 V in phosphoric acid electrolyte, the following can be drawn. Hydrogen that enriches at the anodic niobia/niobium metal interface originates mainly from the hydrogen impurity in metal substrate. Hydrogen species in anodic niobia films are mainly incorporated from electrolyte. (English)

Electropolishing of NiTi Shape Memory Alloys in Methanolic H_2SO_4

K. Fushimi, M. Stratmann, and A.W. Hassel

Electrochim. Acta, **52**, 1290-1295 (2006).

The electropolishing of NiTi shape memory alloys was surveyed electrochemically. Anodic polarization of NiTi up to 8 V was performed in various aqueous and methanolic H_2SO_4 solutions. The passivity could be overcome in methanolic solutions with 0.1 mol $dm^{-3} \leq C_{H2SO4} \leq 7$ mol dm^{-3}. The dissolution kinetics was studied in dependence of the polarization potential, the H_2SO_4-concentration, the water concentration and the temperature. For lower concentrations of sulfuric acids ($C_{H2SO4} \leq 0.3$ mol dm^{-3}) electropolishing conditions were not observed for potentials up to 8 V. The dissolution remained under Ohmic control. In the concentration range from 1 to 7 mol dm^{-3} a potential independent limiting current was registered depending linearly on the logarithm of concentration. The best results were obtained with a 3 mol dm^{-3} methanolic sulfuric acid at 263 K which yielded an electropolishing current of 500 A m^{-2} at a potential of 8 V. Surface roughness as well as current efficiency showed an optimum under these conditions.

Surface Charge of Hardened Cement Paste Determined by Membrane Potential

Y. Elakneswaran, T. Nawa, K. Kurumisawa, and K. Fushimi

Cement Science and Concrete Technology, **60**, 111-117 (2006).

Since hardened cement paste has a variable pore structure in which pores are connected to each other, the transport of ions through the cement paste is inevitably affected by the charge on the pore surface and the diameter of the pores. When two electrolyte solutions are separated by hardened cement paste, a membrane potential develops across the cement paste. This varies according to the electrolyte concentration difference, the surface charge, the pore diameter, porosity and the mobility of the permeating ions in the paste. In this study, the dependences of the water to cement ratio (W/C) and the curing period on the membrane potential of hardened Ordinary Portland Cement (OPC) paste (HCP) were investigated. From the results, membrane potential of HCP in NaCl solution is satisfied Teorell, Meyer and Siveres theory. The surface charge concentration increases with the decrease in the W/C and/or the increase in the curing period and results in an increase in membrane potential. Furthermore, the transport number of the anions in the HCP was larger than of the cations, indicating that HCP has a positive surface charge ad indicates anion selectivity.

Micro-Technology on Aluminum by Anodizing, Laser Irradiation and AFM Probe Processing

S. Kurokawa, Y. Akiyama, M. Yamada, Z. Kato, T. Kikuchi, M. Sakairi, and H. Takahashi

Proc. of ASST 2006

Micro-technologies on aluminum by anodizing with laser irradiation, AFM probe processing, and electrochemical techniques are reviewed. The principle of the technique using laser irradiation is based on the film removal from the aluminum substrate at selected areas by pulsed Nd-YAG laser irradiation, followed by the deposition of metals, resins, and conductive polymers at the film-removed area. Printed circuit boards, electrochemical micro-reactors, plastic-injection molds, free-standing structures, and micro-actuators were fabricated using these techniques.

Micro-patterning of aluminum covered with thin anodic oxide films was carried out by scratching with AFM probe, and the subsequent electrochemical deposition of metals and resins at the film-removed area by scratching. Fabrication of copper dot arrays and acrylic acid- / melamine-resin patterns is described.

Oxide Films on Aluminum by Electrophoretic Sol - Gel Coating / Anodizing

H. Takahashi, M. Sunada, T. Kikuchi, M. Sakairi, and S. Hirai

Passivation of Metals and Semiconductors, and Properties of Thin Oxide Layers,
edited by P. Marcus and V. Maurice, p.685 - 690 (2006)

Highly pure aluminum specimens (99.99 %) with electropolishing or DC-etching were covered with SiO_2 films by electrophoretic sol-gel coating, and were anodized in a neutral borate solution. Time-variations in cell voltage during electrophoretic sol-gel coating and in anode potential during anodizing were monitored. Structure and dielectric properties of the anodic oxide films were examined by SEM, TEM, EDX, and electrochemical impedance spectroscopy.

It was found that electrophoretic sol-gel coating forms uniform SiO_2 films on the surface of both electropolished and DC-etched specimens. Anodizing of specimens after electrophoretic deposition lead to the formation of anodic oxide films consisting of an inner alumina layer and an outer Al-Si composite oxide layer. The anodic oxide films formed thus had slightly higher capacitances than anodic oxide films on aluminum without any coating. Higher heating temperatures after electrophoretic deposition caused the increase in capacitance of anodic oxide films more effectively.

Micro- and Nano-Technology Based on Anodizing

T. Kikuchi, Y. Akiyama, S. Kurokawa, K. Nagahara, M. Sakairi, and H. Takahashi

Mat. Sci. and Eng., **43**, 136 – 141 (2006)

Recent investigations on micro- and nano-technology based on anodizing of aluminum are reviewed, which involve the fabrication of nano-wires and –tubes by depositing metals and compounds into the pores of anodic oxide films, and the combination of anodizing with laser irradiation, AFM probe scratching, and a variety of electrochemical techniques such as electroplating, electroless plating, electrophoretic deposition, electropolymerization. The latter techniques can be applied to fabricate micro-printed circuit boards, plastic injection molds, micro-electrochemical reactors, 3D-micro-structures, 3D-micro-manupilators, micro-metal dot arrays, acrylic acid resin nano-patterns. (in Japanese)

Recent Development of Aluminum Surface Technology Based on Anodizing

H. Takahashi

J. Surf. Fin. Soc. Jpn., **57**, 201 – 208 (2006)

Structure and properties of anodic oxide films on aluminum are reviewed and their application for the experimental fabrication of micro-patterning and -devices. Structural Change of porous type and barrier type anodic oxide films by post-treatments like heating, hydrothermal treatment and re-anodizing and others are also described for the development of novel techniques. Combination of Anodizing with MOCVD, sol-gel dip coating, electrophoretic sol-gel coating can be used for the formation of composite oxide films, which act as dielectric layers in novel electrolytic capacitors with high electric capacitance.

Combination of laser irradiation with a variety of electrochemical techniques such as electroplating, electroless plating, electrophoretic deposition, electropolymerization enables to deposit metals, organic compounds, and electrochonductive polymers at selected areas on aluminum. Using these techniques, micro-printed circuit boards, plastic injection molds, micro-electrochemical reactors, 3D-micro-structures, and 3D-micro-manupilators are fabricated and their performances are examined.

Scratching of aluminum covered with thin barrier type anodic oxide films with probe of atomic force microscope allows to make nano-sized patterns. Combining the AFM probe scratching with electroplating and electrophoretic deposition, metal dot arrays and acrylic acid resin nano-patterns are fabricated. (in Japanese)

Effect of Porous Type Anodic Oxide Film Thickness on Galvanic Corrosion of Aluminum Alloys

M. Sakairi, Y. Shimoyama and H. Takahashi

ATB Metallurgie, **45**,285-289 (2006)

A new type of electrochemical noise analysis technique was applied to galvanic corrosion of barrier and porous type anodic oxide films formed on 1100-H14 aluminum alloy in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solutions with 0.3 kmol/m^3 NaCl. The effect of porous type anodic oxide film thickness on galvanic corrosion resistance was also examined. During incubation period (before localized corrosion started), both current and potential slightly change as initial value with time. The incubation period of porous type anodic oxide film formed samples are longer than that of barrier type anodic oxide film samples. The incubation period of porous type anodic oxide specimens become longer with longer anodizing time, thicker porous layer. During localized corrosion, the current and potential were changed, with fluctuations and the potential and the current fluctuations show good correlation.

Initial stage of localized corrosion in artificial pits formed with photon rupture on Zn-55 mass% Al coated steels

M.Sakairi, Y. Uchida and H. Takahashi

ISIJ Int., **46**, 1218-1222 (2006)

The photon rupture method, whose oxide film and metal are removed by focused pulsed Nd - YAG laser beam irradiation was applied to form artificial micro pits in zinc - 55 mass% aluminum coated steels. The 15 μm coated layer was removed by 2 s of continuous laser irradiation in this experiment. The rest potential transients were measured during the laser irradiation. While the coated layer covered the steel substrate, the rest potential change in the negative direction just after the starts of the laser irradiation and then returned to the previous value. However, after the steel substrate was exposed to solution, the rest potential moved in the positive direction immediately after the discontinuation of the laser irradiation and then also returned to the previous value. The amplitude and duration of the potential changes after the laser irradiation increased with longer irradiation, related to the pit depth and exposed area ratio of coated layer / steel substrate. These rest potential fluctuation differences can be explained by galvanic reaction changes in the artificial pit formed on the coated steel during irradiation.

Electrochemical Noise Analysis of Galvanic Corrosion of Anodized Aluminum in Chloride Environments

M. Sakairi, Y. Shimoyama and H. Takahashi

Electrochemistry. **74**, 458-462 (2006)

A new type of electrochemical noise analysis technique with First Fourier Transformation, FFT, was applied to galvanic corrosion of barrier and porous type anodic oxide films formed on aluminum in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solutions with 0.01 kmol/m^3 NaCl. During localized corrosion, the current and potential were changed, with fluctuations and the potential and the current fluctuations show good correlation. The slope of the PSD spectra of both types of anodized specimens are about minus one (-1), just after localized corrosion started. This technique allows observation of electrochemical impedance changes during localized corrosion. The impedance spectra are independent of signal frequency and the impedance of porous types anodic oxide film specimens decrease with immersion time and increases with anodizing time

Localized corrosion of Zinc Alloy Coated Steels in Chloride Ions Containing Solutions with photon rupture method

M. Sakairi, K. Itabashi, Y. Uchida and H. Takahashi

Tetsu-to-Hagane, **92**,16-22 (2006)

A photon rupture method, film removal by a focused one pulse of pulsed Nd- YAG laser beam irradiation, has been applied to investigate initial stage of localized dissolution of Zn and Zn- Al alloy coated steels, which were formed nitrocellulose films as a protective film, in 0.5 kmol m^{-3} H_3BO_3 - 0.05 kmol m^{-3} $Na_2B_4O_7$ (pH = 7.4) with 0.01 kmol m^{-3} chloride ions. This method can remove oxide films and nitrocellulose films on coated layer by laser ablation without any contamination from film removing tools, and the removing speed is extremely high. At low applied potentials, all samples reformed oxide film after films were removed by this method. The oxide film formation kinetics follows on inverse logarithmic law in agreement with Cabrera-Mott theory. However, as increasing applied potential, after some period, localized dissolution occur at nitrocellulose films were removed area. The peak currents of Zn - 55 mass % Al coated steel specimens were larger than those of Zn and Zn - 5 mass% Al coated specimens. This result suggest that high aluminum containing coated layer does not show good corrosion resistance in frequently oxide film removal environments. (Japanese)

Initial Stage Of Localized Corrosion In Artificial Pit Formed On Zinc Coated Steels
By Photon Rupture

Sakairi Masatoshi, Uchida Yoshiyuki and Takahashi Hideaki

Passivation of metals and semiconductors, and properties of thin oxide layers,
P. Marcus and V. Maurice (Edits.) Elsevier B.V.B.V. Oxford, U. K., 561-566
(2006)

Photon rupture method, oxide film and metal removal by focused pulsed Nd YAG laser beam irradiation, has been applied to form artificial micro pit in zinc coated steels. It takes about 2 s to remove zinc coated layer which thickness is about 20 μm by continuous laser irradiation at optimaum laser power. The rest potential transient was measured during laser irradiation.

The rest potential was changed to noble direction just after laser was irradiated and then returned to previous value during zinc covered on the steel. However, after the steel substrate was exposed to the solution, the rest potential move to positive direction just after laser was irradiated and then returned to previous value. The amplitude and duration of potential change after laser irradiation increase with increasing irradiation period which related to pit depth and exposed area ratio of zinc / steel substrate. These rest potential fluctuation difference can be explain by the galvanic reaction change in the artificial pit formed on zinc coated steels during irradiation.

Initial Stage of Localized Corrosion on Titanium in Phosphate Buffer Solutions by Photon Rupture

M. Sakairi, H. Miyata and H. Takahashi

Proc of ECS Transactions, Volume1, Issue4, 183-194 (2006)

A photon rupture method, oxide film removed by focused pulsed Nd-YAG laser beam irradiation, applied to investigate localized repair of passive oxide films of titanium. The specimens were irradiated with a focused pulse of a pulsed Nd - YAG laser beam at a constant potential in 8.1 mol/m^3 Na_2HPO_4/ 5 mol/ｍ^3 KH_2PO_4 solutions with 140 mol/m^3 NaCl + 50 mol/m^3 KCl (PBS) or with different chloride concentrations, and the current transients were monitored. The current increases with increasing applied potential and chloride concentration. The oxide film, however, repair in every experimental conditions. The oxide film formation kinetics did not follow the inverse logarithmic law according to Cabrera-Mott theory.

Electrochemical Noise Study on Galvanic Corrosion of Aluminum Alloy in Chloride Environments
- Effect of Oxide Film Structure

M. Sakairi, Y. Shimoyama and H.Takahashi

Proc of ECS Transactions, Volume, Issue4, 195-206(2006)

Different kind of anodic films, barrier type, porous type anodized in $(COOH)_2$ solutions, porous type anodized in H_2SO_4 solutions and composite type, were formed on the specimen. The effect of anodic oxide film structure on galvanic corrosion of aluminum and its alloys were measured by electrochemical noise technique. During incubation period (before localized corrosion was started), both current and potential slightly changed as initial value with time. After localized corrosion was started, those were suddenly changed with time with fluctuation. The composite type anodic oxide film formed pure aluminum and 6061 alloys showed longest incubation period than another type of anodic oxide film formed specimens. However, anodic oxide treatment did not increase corrosion resistance of 2017 alloy.

Fabrication of Electrochemical Micro-reactor by Photon Rupture Method and Electrochemistry

M. Sakairi, M. Yamada and H. Takahashi

Elecrrochem. Proc. Volume 2004-19, 359-370 (2006)

Photon rupture with a focused single pulse of pulsed YAG-laser irradiation was used to fabricate electrochemical micro-reactor. Porous type anodic oxide film formed specimens were irradiated in solutions with a pulsed Nd-YAG laser beam through a convex lens to fabricate micro channels, micro-electrode and through holes for solution inlet and outlet. During irradiation, specimens were moved by computer controlled XYZ stage. After irradiation, surface of micro-channel and through hole were formed oxide film and it of micro-electrode was formed Au layer by electrochemically. Calculated volume of the micro-reactor including micro-channel and through holes is about 1.5 µl. A cyclic voltammogram of the micro-electrochemical cell was measured in 2 mol/m^3 and 20 mol/m^3 $K_3Fe(CN)_6$ / $K_4Fe(CN)_6$ at static condition at different scanning rate. Anodic and cathodic peak current were measured and these values were depended on scanning rate and ions concentration.

Electrochemical Noise Analysis of Environmental Degradation of Anodized Aluminum

M. Sakairi and Y. Shimoyama

Proc. of The 3rd Korea-Japan Joint Seminar for Capacitor Energy System, 29-35 (2006)

A new type of electrochemical noise analysis technique was applied to environmental degradation, namely, galvanic corrosion of anodic oxide films formed aluminum in NaCl containing 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solutions. The effect of anodic oxide film thickness on galvanic corrosion resistance was also examined. During incubation period (before localized corrosion started), both current and potential slightly change as initial value with time. The incubation period of porous type anodic oxide specimens become longer with longer anodizing time, thicker porous layer. During localized corrosion, the current and potential were changed, with fluctuations and the potential and the current fluctuations show good correlation. The slope of the PSD of both potential and current spectra of anodized specimens are about minus one (-1), after localized corrosion started. This technique allows observation of electrochemical impedance changes during localized corrosion.

Electrochemical Noise Analysis During Galvanic Corrosion Of Anodized Aluminum

M. Sakairi, and Y. Shimoyama

Proc. of ISEM Sapporo, B6-1, (2006)

A new type of electrochemical noise analysis technique was applied to galvanic corrosion of anodic oxide films formed 6061-T6 aluminum alloy in NaCl containing 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solutions. The effect of anodic oxide film structure on galvanic corrosion resistance was also examined. During incubation period (before localized corrosion started), both current and potential slightly change as initial value with time. The incubation period of porous type anodic oxide specimens are longer than that of barrier type anodic oxide specimens. During localized corrosion, the current and potential were changed, with fluctuations and the potential and the current fluctuations show a correlation. The slope of the PSD of both potential spectra of anodized specimens are about minus one (-1), after localized corrosion started. This technique allows observation of electrochemical impedance changes during localized corrosion.

FGM's for Biomedical Applications

F.Watari, S.Liao, A.Yokoyama, M.Omori, N.Ohata

Advances in Science and Technology **45**, 1124-1133 (2006)

Functionally graded materials (FGM) were fabricated for bio-medical applications, (1) implants, (2) dental core and post, (3) guided tissue regeneration (GTR) membranes.

(1) FGM implants of Ti/HAP and TiN/HAP with the concentration changing gradually in the longitudinal direction of cylinder were fabricated to optimize both mechanical properties and biocompatibility in each region. Concentration gradient was formed by packing of dry powders into mold. Spark plasma sintering was effective for sintering of non-uniform composition in FGM. Brinel hardness decreased gradually from Ti part to HAP part, which contributes to stress relaxation in the implanted region of bone. In vivo tests showed that osteogenesis and maturation is more advanced in the HAP rich region.

(2) FGM dental core and post made of composite resin was fabricated by laser lithography, one of the photo-curing type CAD/CAM systems. The elastic modulus changed gradually from 10.6GPa in core part to 2.9GPa at the apex of post by decreasing the filler content of ceramic powders from 64% to 0% in polymer matrix. Stress analysis using finite element method showed the stress relaxation by further 30 % in FGM, compared with the uniform composite resin.

(3) Biodegradable GTR membrane composed of nano HAP/collagen reinforced with PLGA was prepared. The membrane has the three layer structure with the thickness of about 100mm for each where the composition of HAP/collagen is increased from pure PLGA. The graded membrane structure could give the different functions of the high degradation speed and Ca ion release to enhance osteoconductivity for bone remodeling in the high HAP/collagen side and the relatively low degradability to prevent the ingrowth of fibroblasts in the pure PLGA side.

Comparison of Morphology and behavior of carbon nanotubes and asbestos

F.Watari, M.Inoue, T.Akasaka, N.Sakaguchi, H.Ichinose, and M.Uo

Proc.6th Asian BioCeramics Symp.2006, 142-145 (2006)

Carbon nanotubes (CNT) have attracted up to now the attentions to the application in the electronic and chemical fields. However the application for the biomedical field has been very rare. There are arguments that CNT may have the serious toxicity due to its acicular or fibrous particle shape, associated with lung carcinogenicity of asbestos. In this study we compared the morphology and behavior of CNT and asbestos, including chrysotile (white asbestos), crocidolite (blue asbestos), and amosite (brown asbestos). Crocidolite and amosite, which have stronger carcinogenicity, show the acute acicular form with much Fe elemental content, while chrysotile and CNT have a wavy fibrous form. CNT is especially flexible and easily winding around small objects of even m or less such as bacteria or fine asbestos fibers. Asbestos is hydrophilic and small crystallites are easily dispersible, while CNT is hydrophobic and easily agglomerated, which often causes difficulty to scatter for various applications. We have rather found the favorite properties as biomaterials in CNTs such as affinity for saccharides and proteins, cell adhesion, bacteria adsorption and apatite precipitation, some of which are very different from graphite, one of the isomorphs of CNT. Although the particle size allows the possibility to attain pulmonary alveolus through the respiratory system for both CNT and asbestos, the chemical properties and bio-environmental behavior of CNT seem different from asbestos.

Effect of surface condition of dental zirconia ceramic (Denzir) on bonding

M. Uo, G. Sjögren, A. Sundh, M. Goto, F. Watari and M. Bergman

Dental Materials Journal, **25**, 626-31 (2006)

Yttria partially-stabilized zirconia (YPSZ) ceramics are suitable for dental and medical use because of their high fracture toughness and chemical durability. The purpose of this study was to examine the bonding of a dental YPSZ ceramic (Denzir). After being subjected to various surface treatments the Denzir specimens were bonded to each other using an adhesive resin composite, glass ionomer or zinc phosphate cement. The bonding strength was then determined by the shearing test. No significant difference ($p > 0.05$) was observed between SiC- and Al_2O_3-blasted specimens. In all surface treatments, the shear bonding strength significantly ($p < 0.05$) increased in the order of adhesive resin composite cement > glass ionomer cement > zinc phosphate cement. Silanization with methacryloxy propyl trimethoxysilane slightly increased the bonding strength of the adhesive resin composite.

Selenium distribution in human soft tissue determined by using X-ray scanning analytical microscope and X-ray absorption fine structure analysis

M. Uo, K. Asakura, T. Kohgo and F. Watari1

Chemistry Letters **35**, 66-7 (2006)

Se localilzation in the human oral mucosae which contain dental amalgam or dental silver alloy particles was analyzed by X-ray scanning analytical microscopy (XSAM). Se distribution was visualized, and the localization in the neighbor of amalgam or silver particles was confirmed. The chemical state of Se was analyzed by X-ray absorption fine structure (XAFS) analysis. Se was estimated as the low valency state. The possibility of using XSAM and XAFS for the analysis of the distribution and chemical state of rarely contained elements in biological tissue was suggested.

Apatite formation on carbon nanotubes

T.Akasaka, F.Watari, Y.Sato and K.Tohji

Materilas Science and Engineering C, **26**, 675-78 (2006)

Apatite coating on carbon nanotubes (CNTs) was done with a biomimetic coating method. The multi-walled CNTs (MWNTs) of curled shape with about 30 nm in diameter were immersed for 2 weeks in the simulated body fluid. Observation by scanning electron microscopy (SEM) showed the formation of apatite on the MWNTs surface. The clusters of spherules consisting of needle-shaped apatite crystallites were massively grown on the aggregated MWNTs. The crystallites of 100 nm in width and 200–500 nm in length were grown perpendicularly to the longitudinal direction and radially originating from a common center of a single MWNT. Thus, the architecture of crystalline apatite at nano-scale levels could be produced by simple method and the MWNT may be acting as core for initial crystallization of apatite.

Spectral shifts of ozone molecule by the complex formation with a water molecule

H. Tachikawa, and S. Abe

Chem. Phys. Lett, **432**, 409-413 (2006)

The excitation energies of O_3–H_2O complex have been calculated by means of SAC–CI method to elucidate the spectral shifts of excitation energies of O_3 caused by the complex formation with a water molecule. The eclipsed form, where the center oxygen of O_3 and water oxygen are located on the C_s molecular plane, was examined in the present study. The first and third excitation energies of O_3 were slightly blue-shifted by the complex formation with H_2O. The oscillator strength for the third excitation was not affected by the complex formation, indicating that the photo-dissociation of the O_3–H_2O complex occurs efficiently as well as free ozone molecule. The electronic states of the complex was discussed on the basis of theoretical results.

Strikingly Extended Morphology of Cells Grown on Carbon Nanotubes

N. Aoki, A. Yokoyama, Y. Nodasaka, T. Akasaka, M. Uo, Y. Sato, K. Tohji and F. Watari

Chemistry Letters **35**, 508-9 (2006)

The morphology of cells cultured on carbon nanotube (CNTs) scaffolds was investigated using a confocal laser scanning microscope (CLSM) and a scanning electron microscope (SEM) and it was shown that the cells extended strikingly in all directions and numerous filopodia extended far from the cells.

X-ray absorption fine structure (XAFS) analyses of Ni species trapped in graphene sheet of carbon nanofibers

M. Ushiro, K. Uno, T. Fujikawa, Y. Sato, K. Tohji, F. Watari, WJ. Chun, Y. Koike , K. Asakura

Physical Review B, **73**, 144103-1-11 (2006)

Metal impurities in the carbon nanotubes and carbon nanofibers play an important role in understanding their physical and chemical properties. We apply the Ni *K*-edge x-ray absorption fine structure analyses to the local electronic and geometric structures around embedded Ni impurities used as catalysts in a carbon nanofiber in combination with multiple scattering analyses. We find almost Ni catalysts as metal particles are removed by the purification treatment. Even after the purification, residual 100 ppm Ni species are still absorbed; most of them are in monomer structure with Ni-C bond length 1.83 Å, and each of them is substituted for a carbon atom in a graphene sheet.

TDS Measurement of Hydrogen Released from Stainless Steel Oxidized in H_2O-Containing Atmospheres

A. Yamauchi, Y. Yamauchi, Y. Hirohata, T. Hino and K. Kurokawa

Materials Science Forum, **522-523**, 163-170(2006)

Hydrogen dissolved in the Cr_2O_3 scale formed on the stainless steel in the H_2O-containing atmospheres is observed by TDS (thermal desorption spectroscopy) measurements. The amount of dissolved hydrogen in the Cr_2O_3 scale reaches a maximum about 0.32 mol% when the H_2O concentration in the gas reaches 20%. It was found from GDS (glow discharge spectroscopy) measurements that hydrogen may exist at the oxide scale / substrate interface or in Cr_2O_3 scale bounded that interface. However, results from the Vickers hardness and the observation of scale morphology by SEM (scanning electron microscopy), hydrogen dissolved in the Cr_2O_3 scale would have little effect on a decrease in the mechanical property of the Cr_2O_3 scale. Therefore, hydrogen dissolved in the Cr_2O_3 scale may not be main factor of the deterioration of the Cr_2O_3 scale.

Microstructures of SiO_2 scales formed on $MoSi_2$

K. Kurokawa, D. Goto, J. Kuchino, A. Yamauchi, T. Shibayama and H. Takahashi

Materials Science Forum, **522-523**, 595-601(2006)

The microstructures of oxide scales formed on $MoSi_2$ at medium-high temperatures in air were observed by TEM. Based on the observation, relationships between oxidation temperature and formation of MoO_3 and crystallization of amorphous SiO_2 scales were investigated. At 1273 K and 1373 K, the oxide scales had a structure consisting of amorphous SiO_2 with small amounts of fine MoO_3 particles. The oxide scales at 1573 K and 1773 K had a structure consisting of amorphous and crystalline SiO_2. Growth rate of the oxide scale formed at 1773 K appreciably increased due to crystallization of amorphous SiO_2. It was thought that the increase in the oxidation rate at 1773 K was caused by a change in the diffusion mechanism from O_2 diffusion to lattice diffusion of O^{2-} through SiO_2. In addition, the diffusion coefficient of oxygen was estimated from the growth rate of SiO_2 scale.

Nanoscale surface self-patterning of FeAl single crystals by vacancy absorption process

K. Yoshimi, M. Tsunekane, R. Nakamura, A. Yamauchi and S. Hanada

APPLIED PHYSICS LETTERS, **89**, 073110 1-3 (2006)

The surface morphology of B_2-structured FeAl single crystals is modified on a nanoscale by the absorption process of supersaturated thermal vacancies. A high density of nano to mesoscale surface pores is successfully produced by the vacancy absorption process through water quenching, surface treatments, and aging heat treatment. Their shape, size, and density can be controlled by varying the surface orientation of single crystals, quenching temperature, aging temperature, and aging time. These results suggest that surface self-patterning by the vacancy absorption process is a useful bottom-up technique for obtaining nanoscale surface patterns in metallic materials.

Structure and oxidation resistance of plasma sprayed Ni–Si coatings on carbon steel

Y. N. Wu, Y. Kawahara and K. Kurokawa

Vacuum, **80**, 1256–1260 (2006)

Ni–Si coatings consisting of mainly $NiSi_2$ and NiSi were deposited on a carbon steel by air plasma spraying. Isothermal oxidation tests of the carbon steel substrates with the Ni–Si coatings at 500–800℃ have been carried out. The result indicated that a protective SiO_2-based oxide scale was formed on the surface of the coatings after oxidation. On the other hand, during oxidation, phase transformation occurred among the $NiSi_2$, NiSi and Ni_2Si phases constructing the Ni–Si coatings. This was caused by the extraction of silicon from the silicides and the reformation of silicides at the silcide/Si-blocks interface. Above 700℃, the outward diffusion of iron and carbon became very fast and consequently decarburization happened at the coating/substrates interface, which induced the formation of pores in the substrates near the interface. In addition, grain boundary oxidation of Cr in the steel substrate was observed above 700℃.

Effect of Zr Addition on Spalling Rresistance of Al_2O_3 Scale Formed on β-Ni (Al, Cr) Alloys.

H. Tomoto, A. Yamauchi, T. Shibayama, S. Watanabe, K. Kurokawa and T. Narita

Applied Plasma Science, **14**, 87-93 (2006)

In order to investigate the spalling behavior of Al_2O_3 scales formed on β-Ni (Al, Cr) and β- Ni (Al, Cr)-Zr, the effect of Zr addition on the microstructure of Al_2O_3 scale was examined by SEM, TEM and GDS. The isothermal oxidation tests were carried out for up to 360 ks at 1373K in air. The addition of Cr to NiAl alloy led to increase in oxidation rate and the formation of voids in the oxide scale/substrate interface, resulting in promotion of spalling of the Al_2O_3 scale. On the other hand, in the Zr added alloy, the formation of voids in the oxide scale/substrate interface was remarkable suppressed. Thus, Zr addition resulted in the improvement of the adherence of an Al_2O_3 scale to substrate. This improvement may be due to Zr segregation in the oxide scale/substrate interface.

Effect of Alloying Element on Microstructure of NiAl-X/Oxide Scale Interface

S. Kawata, K. Kurokawa, A. Yamauchi, S. Watanabe and T. Narita

J. High Temp. Soc, **32**, 118-122 (2006)

In order to clarify spalling mechanism of oxide scale on NiAl, microstructures in the vicinity of NiAl-X (Hf, Zr) /oxide scale interface were observed by using TEM. The oxidation tests were done at 1373K in air for up to 360 ks. In NiAl, many voids were formed at the substrate/Al_2O_3 interface, leading to spalling of the alumina scale. On the other hand, addition of Hf or Zr to NiAl led to suppression of the void formation, resulting in prevention of spalling of alumina scale. In addition, a Ni-Al-O layer tended to be formed at the interface in NiAl. This demonstrates appreciable increase in oxygen partial pressure and nickel activity at the interface. In face, GDS measurements indicated depression of the Al concentration in the substrate close to an alumina scale. Consequently, it was speculated that the addition of Hf or Zr led to increase in diffusivity of Al in the substrate and suppression of void formation at NiAl/alumina scale, resulting in prevention of spalling of an alumina scale.

Mechanism of Crack Propagation for Cycle Fatigue of Lead-Free Solder Joint

H. Mizuno, J. Tanaka, T. Narita, K. Kurokawa

Proc. of 12th Symposium on “Microjoining and Assembly Technology in Electronics”, 229-234 (2006)

The practical use of various lead-free solder is advanced. As it is now, reliability under the thermal fatigue environment in the electronic substrate solder joint part is hoped for. Especially, the behavior clarification of the crack propagation in the solder initiated by the thermal cycle stress has a big meaning to create new lead-free solder. In this study, after thermal cycle fatigue stress loading to the destruction side of the sample peeled off, and the crack fracture form was observed by the solder composition. Furthermore, the tensile test and the fatigue test are done to survey the initiation site of the crack propagated, and the causal relation between the microstructure and the crack is examined.

Oxidation Behavior of Ni-3, 6, 10wt.% Al Alloys at 800 °C

S. Hayashi, S. Narita, and T. Narita

Oxidation of Metals, **66**, 191-206 (2006)

The oxidation behavior of Ni and Ni-3, 6, and 10Al alloys at 800°C in an N_2–O_2 gas mixture was investigated. The mass gain of each alloy depended on both the oxidation periods and Al content. NiO scale was formed on all alloy substrates accompanied by internal oxides of Al_2O_3. Many cavities were formed at the NiO/substrate interface at shorter oxidation times, and these cavities were found to be filled by metallic Ni(Al) from the matrix in the internal-oxidation zone by the development of internal oxides. The filling of cavities by Ni(Al) was more significant on higher Al alloys, which had a higher density of internal Al_2O_3. Once metallic Ni(Al) formed along the entire NiO/substrate interface, the oxidation kinetics became the same as pure Ni. It was concluded that pure Ni filling the cavities at the interface provided a diffusion path of Ni from the substrate to the NiO scale, and that controlled the oxidation kinetics.

High Temperature Oxidation Resistant Coatings -Coating design from a chemical potential and interdiffusion perspective-

S. Hayashi and T. Narita

Zairyo to Kankyo, **55**, 476-482 (2006)

Recent requirement for increasing operation temperatures in energy conversion system has let to an increase in the demand for improving materials at higher temperatures. Coating in one method used to meet these demands by retaining substrate mechanical properties and giving improved high temperature oxidation and corrosion resistance. This review introduces some recent results we obtained, and concept for next generation coatings are discussed.

Development of Fuel Clad Materials for High Burn-up Operation of LWR.

Cho Hang-Sik, A. Kimura, S. Ukai, M. Fujiwara

ASTM Special Technical Publication (2006), STP 1475,
Effects of Radiation on Materials: 22nd Symposium), 111-119.

Oxide dispersion strengthening (ODS) steels have been considered to be very promising for fuel clad materials for high burn-up operation of light water reactor and super crit. water reactor. For improving the corrosion resistance, increasing chromium concn., which often resulted in degrdn. of mech. properties and thermal embrittlement, has been required. In this work, the effects of aluminum addn. on the mech. properties of high chromium ODS steels have been investigated. Various ODS steels which have 14 .apprx. 22 wt% Cr concns. were made by mech. alloying method. In order to evaluate the mech. properties and the effect of thermal aging, a miniaturized Charpy V notch test and tensile test were performed before and after aging. (1) The addn. of Al resulted in the decrease in anisotropy of tensile properties, although it reduced the tensile stress. (2) The impact properties of 19Cr-ODS steel are improved by the addn. of A1.

Microstructural Examination of Oxide Layers Formed on an Oxide Dispersion Strengthened Ferritic Steel Exposed to Supercritical Water

Y. Chen, K. Sridharan, T. R. Allen, and S. Ukai

Journal of Nuclear Materials (2006), **359**(1-2), 50-58.

A TEM study was carried out on the oxide layers formed on a 9Cr oxide dispersion strengthened (ODS) ferritic steel after exposure to supercrit. H2O at 500□ with a 25 ppb dissolved O concn. Compared with the oxide layers formed on a conventional 9Cr steel NF616 ferritic steel with a similar major element compn. and exposed to similar test conditions, the 9Cr ODS steel exhibited a different oxide structural morphol. and growth mechanism. The most pronounced difference was the development of a substantially thick internal oxidn. layer for the ODS steel that is assocd. with its finer grain size. For the oxidized ODS steel, Y and Cr rich oxide ribbons formed at the steel grain boundaries in the internal oxidn. layer. The improved overall corrosion resistance of 9Cr ODS steel at elevated temps., as measured by wt. gain data, may be a result of Y acting as a barrier for cation diffusion along oxide/metal grain boundaries. The gradual decrease in scale d. with increasing exposure times appears to be caused by depletion of Fe, which resulted in more vacancies and pores in the inner (FeCr)3O4 spinel layer.

Corrosion of Candidate Materials for Supercritical Water-Cooled Reactors

T. R. Allen, Y. Chen, L. R. Tan, K. X. Sridharan, and S. Ukai

Proceedings of Sessions and Symposia held during the TMS Annual Meeting, San Antonio, TX, United States,
Mar. 12-16, 2006 (2006), 1397-1406. Publisher: Minerals, Metals & Materials Society

Advanced nuclear energy systems have been proposed that will use supercrit. water as a coolant. Because of the limited experience with candidate alloys exposed to supercrit. water, a test program has been initiated to understand oxidn. behavior in these candidate alloys. This work will report on the corrosion response of two austenitic and three ferritic-martensitic steels exposed to supercrit. water at a temp. of 500 C and 25 ppb dissolved oxygen content up to exposure times of 1026 h. The alloys tested and examd. were 800H, D9, NF616, HCM12A, and an Oxide Dispersion Strengthened (ODS) martensitic steel contg. 9% Cr. Following exposure, wt. change was measured and the oxide was characterized. Ferritic-martensitic steels experienced a larger wt. gain than austenitic stainless steels, but the oxide growth is more predictable for the ferritic-martensitic steels. The ODS steel showed significantly less oxidn. than the other ferritic-martensitic alloys. Both D9 and alloy 800H showed spallation of the oxide. Thermo-mech. processing of 800H was used to maximize the fraction of low angle grain boundaries. This treatment significantly improved the oxidn. response in 800H. There was an enrichment of hematite in the outer oxide layer and an improvement in oxide adhesion to the substrate, which appears to be linked to a redn. in anisotropy in the oxide.

Nano-Mesoscopic Structural Control in 9CrODS Ferritic/Martensitic Steels

S. Ohtsuka, S. Ukai, and M. Fujiwara

Journal of Nuclear Materials (2006), **351**(1-3), 241-246.

Effects of varying O concn. and final heat treatment on high-temp. strength and microstructure in 9Cr-oxide dispersion strengthened steel (9CrODS) were studied in view of fast reactor application. Appropriate control of excess O concn. remarkably improves creep strength of 9CrODS. This creep strength improvement is ascribed to ultra-fine oxide particle dispersion in a part of the grains and increasing austenite to ferrite diffusional transformation. Enhancement of austenite to ferrite diffusional transformation leads to suppression of grain boundary sliding. Creep strength of 9CrODS can be remarkably improved by controlling excess O concn. and performing a furnace-cooling heat treatment for austenite to ferrite diffusional transformation

Ferritic Steel-Blanket Systems Integration R&D-Compatibility Assessment

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Fusion Engineering and Design (2006), **81**(8-14), 909-916.

A review. The reduced activation ferritic steel (RAFS) was selected as structural material for a variety of blanket systems for ITER test blanket modules (TBM). In the evaluation of integrated performance of ferritic steels as structural components of blanket systems, there are unique issues as well as common issues for each blanket system. One of the unique issues for each system is the compatibility of ferritic steels with the coolant materials. The corrosion rate of ferritic steels in hot H2O, super crit. pressurized H2O (SCPW), humid air, Pb-17Li, Li and Flibe at various temps. is reviewed. Efforts to improve corrosion resistance have been made, taking the alloy design into account. A dispersion of yttria was effective to improve corrosion resistance of a RAFS. The compatibilities of RAFSs with hot H2O, Pb-17Li, Li and Flibe are considered to be good enough for the TBM applications. The liq. metal embrittlement (LME) is considered to be a crit. issue for the use of RAFSs for the Li systems. Several issues towards DEMO and beyond are shown from the compatibility point of view.

Improvement of Compatibility of Advanced Ferritic Steels with Super Critical Pressurized Water Toward a Higher Thermally Efficient Water-Cooled Blanket System

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Fusion Engineering and Design. (2006), **81**(8-14), 1071-1076.

Various oxide dispersion strengthened (ODS) steels which have high Cr concns. with and without Al addn. were made by mech. alloying method. Corrosion measurement was done in the closed system of super crit. pressurized water (SCPW) at 783 K with the pressure of 25 MPa. In order to evaluate the mech. properties and the effect of thermal aging, a miniaturized Charpy V notch (MCVN) test and tensile test were performed before and after aging at 773 K up to 1000 h. The susceptibility to stress corrosion cracking (SCC) of high Cr-ODS steels was evaluated by slow strain rate test (SSRT). The SSRT was performed in a simulated boiling water reactor (BWR) condition with high temp. oxygenated (8-10 ppm) water at 561 K and at a pressure of 7.8 MPa. Strain rates were ranging from 1 x 10^{-4} to 3 x 10^{-7} s^{-1}. The high Cr-ODS steels showed a better resistance to corrosion than SUS316L stainless steel in SCPW. The 14Cr and 16Cr-ODS steel did not suffer from aging embrittlement at 773 K for 1000 h. The ODS steels showed no susceptibility to SCC at strain rates from 1 x 10^{-4} to 3 x 10^{-7} s^{-1}.

Microstructural Evolution during Creep of 9Cr-ODS Steels

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Fusion Engineering and Design. (2006), **81**(8-14), 1013-1018.

9Cr-ODS (oxide dispersion strengthened) steels are being developed for structural materials of fast breeder reactors and fusion reactors. The steels can be characterized by small Y-Ti-O complex oxide particles dispersed in the matrix. Thus, many researches have studied creep properties by focusing on oxide particles and dislocations with TEM observations, but such studies are still insufficient to clarify the creep mechanism. A potential microstructural feature affecting creep properties, prior particle boundary (PPB) cavities formed during creep and aligned along the extrusion direction, was studied. Field emission gun-SEM (FE-SEM) observations on the crept specimens indicated PPB cavities enhanced creep crack propagation. The effect of PPB cavities on creep properties were quant. studied by consolidating 2 different sizes mech. alloying (MA) powders (>90 and <45 μm). PPB cavities decreased when using the larger MA powder and creep properties parallel to the extrusion direction were improved. PPB is one of the important microstructural features affecting creep properties, where a redn. in PPB cavities signifies an improvement.

Advanced Coatings on High Temperature Applications

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Materials Science Forum, **522-523**, 1-14 (2006)

To suppress interdiffusion between the coating and alloy substrate in addition to ensuring slow oxide growth at very high temperature advanced coatings were developed, and they were classified into four groups, (1) the diffusion barrier coating with a duplex layer structure, an inner σ-(Re, Cr, Ni) phase as a diffusion barrier and outer Ni aluminides as an aluminum reservoir formed on a Ni based superalloy, Hastelloy X and Ni-based alloy. (2) the up-hill diffusion coating with a duplex layer structure, an inner $TiAl_2$+$L1_2$ and an outer β-NiAl formed on TiAl intermetallic and Ti-based heat resistant alloys by the Ni-plating followed by high Al-activity pack cementation. (3) the chemical barrier coating with a duplex layer structure, an inner γ+β+Laves three phases mixture as a chemical diffusion barrier and outer Al-rich γ-TiAl as an Al reservoir formed by the two step Cr/Al pack process. (4) the self-formed coating with the duplex structure, an inner α-Cr layer as a diffusion barrier and an outer β-NiAl as an Al-reservoir on Ni-(20～50)at%Cr alloy changed from the δ-Ni_2Al_3 coating during oxidation at high temperature. The oxidation properties of the coated alloys were investigated at temperature between 1173 and 1573K in air for up to 1,000hrs (10,000hrs for the up-hill diffusion coating). In the diffusion barrier coating the Re-Cr-Ni alloy layer was stable, existing between the Ni-based superalloy (or Hastelloy X) and Ni aluminides containing 12～50at%Al when oxidized at 1423K for up to 1800ks. It was found that the Re-Cr-Ni alloy acts as a diffusion barrier for both the in ward diffusion of Al and outward diffusion of alloying elements in the alloy substrate. In the chemical barrier coating both the $TiAl_2$ outermost and Al-rich γ-TiAl outer layer maintained high Al contents, forming a protective Al_2O_3 scale, and it seems that the inner, γ, β, Laves three phase mixture layer suppress mutual diffusion between the alloy substrate and the outer/outermost layer.

Effect of Coatings on the Creep and Oxidation Behavior of TiAl Alloys at 1173K in Air

T. Nishimoto, S. Hayashi and T. Narita

Materials Science Forum, **522-523**, 665-672 (2006)

The effects of coatings on the creep and oxidation behavior of Ti-50Al alloy were investigated at 1173K in air at a constant loading of 30MPa. The coating was formed by a two-step Cr/Al diffusion treatment and consisted of an outermost $TiAl_2$ layer, an outer Al-rich γ layer, an intermediate γ, Laves and β mixture layer, and a Cr diffusion zone. Creep tests were also carried out with sole Cr or Al coated TiAl and also of uncoated TiAl. The oxide scales formed on the uncoated TiAl and the sole Cr coated specimens were a mixture of TiO_2 and Al_2O_3, which displayed several exfoliations. Both the two-step Cr/Al coated TiAl and the sole Al coated specimens formed a protective Al_2O_3 layer and little oxide exfoliation was observed here. Significant cracks were observed in the sole Al coated TiAl, while no cracks were observed in the sole Cr coated TiAl; the two-step Cr/Al coated TiAl showed a number of cracks in the coatings. Low creep rates in the two-step Cr/Al coated TiAl could be due to the Laves phase with a hexagonal C14 structure in the intermediate, γ, β and Laves phase mixture, and the high creep rates of the sole Cr coated TiAl may originate in the major β phase component with a B2 structure in theγ, β and Laves phase mixture.

Formation of Hydrotalcite in Aqueous Solutions and Intercalation of ATP by Anion Exchange

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Y. Mawatari and M. Tabata

J. Colloid Interface Sci., **300**, 1648-654 (2006)

The formation reaction and the intercalation of adenosine triphosphate (ATP) were studied for hydrotalcite (HT), a layered double hydroxide (LDH) of magnesium and aluminum. Hydrotalcite with nitrate ions in the interlayer (HT-NO_3) was formed (A) by dropwise addition of a solution of magnesium and aluminum nitrates (pH *ca.* 3) to a sodium hydroxide solution (pH *ca.* 14) until the pH decreased from 14 to 10 and (B) by dropwise addition of the NaOH solution to the solution of magnesium and aluminum nitrates with pH increasing from 3 to 10. The precipitate obtained with method (B) was contaminated with aluminum hydroxide and the crystallinity of the product was low, possibly because aluminum hydroxide precipitates at pH 4 or 5 and remains even after HT-NO_3 forms at pH above 8. With method (A), however, the precipitate was pure HT- NO_3 with increased crystallinity, since the solubility of aluminum hydroxide at pH above and around 10 is high as dissolved aluminate anions are stable in this high pH region, and there was no aluminum hydroxide contamination. The formed HT-NO_3 had a composition of $[Mg_{0.71}Al_{0.29}(OH)_2](NO_3)_{0.29} \bullet 0.58H_2O$. To intercalate ATP anions into the HT-NO_3, HT-NO_3 was dispersed in an ATP solution at pH 7. It was found that the interlayer nitrate ions were completely exchanged with ATP anions by ion exchange, and the interlayer distance expanded almost twice with a free space distance of 1.2 nm. The composition of HT-ATP was established as $[Mg_{0.68}Al_{0.32}(OH)_2](ATP)_{0.080} \bullet 0.88H_2O$. The increased distance could be explained with a calculated molecular configuration of the ATP as: An ATP molecule is bound to an interlayer surface with the triphosphate group, the adenosine group bends owing to its bond angles and projects into the interlayer to a height of 1 nm, and the adenosine groups aligned in the interlayer support the interlayer distance. (English)

MO Simulation of Surface Diffusion of Zinc Adatoms on Zinc Surface

K. Iokibe, K. Azumi and M. Seo

ECS Trans. **1**, (4) 279-286 (2006)

Surface diffusion process of zinc adatoms on zinc crystal surface was simulated using semi-empirical molecular orbital (MO) method. Total energy, E_T, of molecular orbitals belong to the system including adatom and surface atoms was calculated for two surface models; one is a small cluster composed from surface atoms and another is periodically repeated arrangement of surface atoms. E_T was calculated as a function of position of adatom on the terrace, near the step and kink sites to draw energy contour map. From the energy map migration path of adatom on the surface and their activation energy for diffusion, E_D, were estimated. From these results adequacy of terrace-step-kink (TSK) model for epitaxial growth was confirmed. Formation of deposition island and effect of water molecule on the surface are also discussed.