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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 films consisting of conductive polymers

A conductive polymer coating was applied to corrosion prevention of carbon 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 steel plate in aqueous solution containing pyrrole monomer. 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 self-healing property of the coated steel was also examined.

The PPy film was also prepared on zinc from tartrate solution containing sodium molybdate and pyrrole monomer. Before formation of the PPy film, a salt layer consisting of zinc tartrate and zinc molybdate is initially formed on the substrate zinc, the layer which works as a passivation layer for zinc.

(2) Monitoring of corrosion products on model cut-edge of zinc alloy coated steels by Raman spectroscopy

Corrosion products on zinc layer coupled with bare steel in atmosphere were studied by Raman spectroscopy under the in-situ and ex-situ condition. At the presence of NaCl precipitate, zinc-hydroxy carbonate was observed on the bare surface, while zinc-hydroxy chloride were detected. The effect on the corrosion products of the amount of the NaCl precipitate and humidity in atmosphere was studied.

(3) Corrosion of Pt-Co and Pd-Co alloy electrode for application of PEFC cathode

As the cathode of PEFC with high performance for the oxygen reduction reaction (ORR), alloying of Co into Pt was proposed. The efficiency of Co addition to Pt and Pd for the ORR and the corrosion of these alloys were studied. The Co addition induced a higher current of the ORR compared with pure Pt and Pd. The surface composition of the alloys reveals a depression of Co which was confirmed by XPS and DGS. The surface oxide was formed in the ORR potential region and it suppressed the ORR current. The surface oxide was measured bu ellipsometry and Raman spectroscopy.

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

Al-Zn-Cr alloy was electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $ZnCl_2$ and $CrCl_2$ for corrosion protection of steel. The electrodeposition was performed by constant potential electrolysis or potential pulse electrolysis. The Zn content in the alloy gradually increases from 2 to 95 at% at potential from -50 to 100 mV (vs. Al/Al(III)). The Cr content increases from 0 to 10 at% at the same potential region. The surface morphology of the deposit was improved by Cr content compare with it of Al-Zn alloy.

(5) Electrodeposition of Bi-Sb-Te alloy 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. The composition of Bi-Sb-Te depended on concentration of Sb ion in electrolyte between 5 and 9 mM. The thin film of $Bi_{0.5}Sb_{1.5}Te_3$ which is thought to be one of the best thermoelectric conversion device was obtained on glassy carbon electrode by pulse potential electrolysis.

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

Glass plates were immersed in a molten salt of $NaNO_3$-$TlNO_3$ at 673-723 K. During the immersion, ion-exchange was induced at the surface of the glass. By the reduction of the glass, Tl ion changed to metallic Tl and then the glass exhibited strong light absorption in visible light from 400 to 700 nm wavelength.

(7) Photoluminescence from passive films of Ni by UV-light excitation

Luminescence light from the anodic thin oxide films formed on Ni in acidic H_2SO_4-Na_2SO_4 solution (pH=2.3) was measured by UV-light irradiation with 3.82 eV energy. The peak wavelength of the luminescence light from the film shows about 410 nm. The wavelength corresponds with the energy at 3.0eV of band gap of NiO.

(8) Characterization of Rust Layer on Weathering Steels

The Rust formed on weathering steel exposed in various sites in Japan fro 17 or 18 years was studied. The absorption of water vapor into the rust was measured by in-situ gravimetry. 8% volume ratio of water was absorbed in the rust layer. The impedance and near IR (NIR) reflectance were also measured during the water absorption. The impedance is decreased and the NIR reflectance is decreased by the insertion of water vapor. The decrease of impedance is influenced by atmosphere of the exposed site. When the site contains relatively large amount of borne salt, the decrease of impedance with the water vapor insertion is more appreciable and the reflectance decrease is also enhanced.

Other Activities

Prof. Ohtsuka and Dr. Kowalski attended the International Conf. on Electrified Interfaces (ICEI 2007), Sahoro, Hokkaido, Japan, June 24-29, 2007 and presents two papers entitled by “Potential modulation reflectance of stainless steels covered by thin passive oxide film” and “The effect of ultrasonic irradiation on polypyrrole film electrodeposition”. Assoc Prof. Ueda attended the Biodegradability and Toxicity of Ionic Liquid meeting (BATIL), Berlin, May 5-9, 2007, and presented a paper entitled by “Anodic dissolution of Ti in EMIC-$AlCl_3$ ionic liquid or LiCl-KCl molten salt for enhancement of adhesion between coating layer and Ti substrate”.

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.

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

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 and 5095 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

High temperature reaction between Al-Mg alloy and pre-roast powder of used dry battery, K. Ta, M. Ueda, T. Ohtsuka and H, Takahashi, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 25-26, 2007

Corrosion process at model edge part of zinc coated steel plate under present of NaCl, Y. Abe, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 25-26, 2007

Corrosion resistance of CoPd and NiPd alloy electrodes as a cathodic electrode in fuel cell, Y. Tamura, 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, February 6-7, 2007

Electrodeposition of Al-Pt alloy in $AlCl_3$-NaCl-KCl molten salt containing $PtCl_2$, H. Hayashi, 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, February 6-7, 2007

Electrodeposition of Al-Zn alloy in chloride and chloride-fluoride molten salt, A. Munekata, 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, February 6-7, 2007

Electrodeposition of Sb-Te compound-semiconductor in chloride molten salt, Y. Mito, 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, February 6-7, 2007

Thickness of passive film on Nd magnet in neutral solution, Y. Nunoko 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, February 6-7, 2007

Formation of conductive polypyrrole film on 55%Al-Zn steel plate, H. Ryu, 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, February 6-7, 2007

Dependence of $SbCl_3$ concentration in molten salt in electrodeposition of Bi-Sb-Te semiconductor, 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, February 6-7, 2007

Corrosion process and corrosion products at cutting edge of zinc coated steel plate, Y, Abe, Symposium of Student of Jpn, Spectroscopy Association Hokkaido Branch, Hokkaido University, Sapporo, February 23, 2007

Thickness measurement of anodic oxide film on Nd-Fe-B permanent magnet by ellipsometry, T. Ohtsuka and Y. Nunoko, Electrochemical Society of Jpn, Faculty of Engineering, Tokyo University of Science, Tokyo, March 29-31, 2007

Electrodeposition of Compound Semiconductor in Molten Salt, M. Ueda, Batil-Meeting, Berlin, Germany, May 5-9, 2007

Application of Synchrotron Radiation to unsolved issues in Research Field in Corrosion, T. Ohtsuka, 2007 Annual Meeting of Jpn Soc. Corros. Eng., Waseda University, Tokyo, May 9-11, 2007

Increase of water absorbance and electric-conductance of rust layer on wethering steel, H. Iwasaki and T. Ohtsuka, 2007 Annual Meeting of Jpn Soc. Corros. Eng., Waseda University, Tokyo, May 9-11, 2007

Theory and experimental results in passive film of metal, T. Ohtsuka、The 9th special lecture for memory of Prof. Go Okamoto, 2007 Annual Meeting of Jpn Soc. Corros. Eng., Waseda University, Tokyo, May 10, 2007

Potential Modulation Reflectance of Stainless steels covered by thin passive oxide film, T. Ohtsuka and Y. Sasaki, International Conf. on Electrified Interfaces (ICEI 2007), Sahoro, Hokkaido, June 24-29, 2007.

The Effect of Ultrasonic Irradiation on Polypyrrole Film Electrodeposition, D. Kowalski, M. ueda, and T. Ohtsuka, International Conf. on Electrified Interfaces (ICEI 2007), Sahoro, Hokkaido, June 24-29, 2007

Characterization of rust layers exhibiting an extraordinarily high corrosion rate, T. Ohtsuka, The 160th Symposium of Corrosion and Protection, Jpn Soc. Corros. Eng., Tokyo, July 6.

Electrochemical measurement of Pd-Co alloy electrode for cathodic oxygen reduction reaction in PEFC, Y. Tamura, K. Taneda, M. Ueda and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 19-20, 2007

Electroplating of Al-Zn-Cr alloys in chloride molten salt, A Munekata, M. Ueda and T, Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 19-20, 2007

Corrosion protection of 55%Al-Zn steel plate by conductive polypyrrole doped with phospho-molybdate ion, H. Ryu, M. Ueda and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 19-20, 2007

Electrodeposition of Sb-Te compound semiconductor in $AlCl_3$-NaCl-KCl molten salt, Y. Mito, M. Ueda and T. Ohtsuka, Hokkaido Branch 2007 Meeting of Chemical Society of Japan, Asahikawa Inst. of tech., Asahikawa, July 21, 2007

Electroplating of Al-Pt alloys in low temperature chloride molten salt, H. Hayashi, M. Ueda and T. Ohtsuka, Hokkaido Branch 2007 Meeting of Chemical Society of Japan,. Asahikawa Inst. of tech., Asahikawa, July 21, 2007

Electrodeposition of Bi-Sb-Te compound semiconductor by control of $SbCl_3$ concentration in molten salt, S. Tsuchiya, M. Ueda and T. Ohtsuka, Hokkaido Branch 2007 Meeting of Chemical Society of Japan,. Asahikawa National College. of tech., Asahikawa, July 21, 2007

EQCM study of the ion exchange behavior of polypyrrole, D. Kowalski, M. Ueda and T. Ohtsuka, Hokkaido Branch 2007 Meeting of Chemical Society of Japan,. Asahikawa National College. of tech., Asahikawa, July 21, 2007

Electroplating of Al alloy in molten salt electrolysis, M. Ueda, Hokkaido Summer

Seminar 2007, Hokkaido University, Sapporo, August 3, 2007

Development of monitoring technique for rust layer on weathering steels by using visible and near-infrared light reflectance, T. Ohtsuka, Symposium of steel structure, Tokyo, September 19, 2007.

Oxygen reduction property of Pd-Co alloy catalytic electrode as a cathodic catalyst of PEFC, K. Taneda, Y. Tamura, M. Ueda and T. Ohtsuka, Fall Meeting, of ECSJ 2007, Tokyo, September 19-20, 2007

Electrochemical measurement of Pd-Co alloy electrode for cathodic oxygen reduction reaction in PEFC, Y. Tamura, K. Taneda, M. Ueda and T. Ohtsuka, Fall Meeting of ECSJ 2007, Tokyo, September 19-20, 2007

Electroplating of Al-Zn-Cr alloys by constant potential electrolysis in chloride molten salt, A. Munekata, M, Ueda and T. Ohtsuka, The116th Annual Meeting of Surf. Finish. Soc. Jpn., Nagasaki University, Nagasaki, September 18-20, 2007

Conductive polypyrrole coating for substitution of chromate coating, T. Ohtsuka and D. Kowalski, The 145th annual fall meeting of ISIJ, Gifu University, Gifu, September 19-21, 2007.

Protection of Zn-55Al alloy coated steel by conductive polypyrrole film doped with molybdate ions, H. Ryu and T. Ohtsuka, The 145th annual fall meeting of ISIJ, Gifu University, Gifu, September 19-21, 2007.

Electroplating of Al-Zn-Cr alloys on mild steel by constant potential electrolysis, A. Munekata, M. Ueda, T. Ohtsuka, The 39th Symposium on Molten Salt Chemistry, Hotel-Matsushima, Matsushima, November 29-30, 2007

Electrodeposition of Bi-Sb-Te alloy by molten salt electrolysis and its thermoelectric properties, S. Tsuchiya, M. Ueda, T. Ohtsuka, The 39th Symposium on Molten Salt Chemistry, Hotel-Matsushima, Matsushima, November 29-30, 2007.

Oxygen reduction reaction of Pt-Co alloy electrodes and their surface state, K. Taneda, Y. Tamura, M. Ueda, and T. Ohtsuka, The 48th battery symposium, Fukuoka, November 13, 2007.

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In June, Dr. Yoshitaka Aoki joined as an Assistant Professor from RIKEN. Professor Emeritus Masahiro Seo, retired in 2006, also joined again as a visiting 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. In addition, we started to tailor functional nanofilms by a chemical process.

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 modification of the anodic films by incorporation of alloying elements is a key issue to improve the dielectric properties. Advanced process using physical vapor deposition has now been investigated to develop a porous electrode for electrolytic capacitor application.

(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 sapphire micro-indenter downward to and upward from the passive surface, a couple of anodic current peaks emerge. The current peaks spiked during both loadings were responsible for partial exposure of substrate metal to the solution due to rupture of the passive film during the indenter tip driving and ascribed to repair the passive film at the ruptured sites. Appearance of current peak during downward indentation was numerically simulated for well understanding of film rupture behavior. The repeated indentation was also performed to investigate the effects of surface transformation to current transients.

(7) Hydrodynamics of Mass-transfer Process in Flowing-electrolyte Type Scanning-droplet-cell

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. Mass-transfer condition was accelerated by flowing electrolyte solution in the droplet cell. Hydrodynamics in the cell was investigated to obtain an experimental limiting current equation.

(8) Scanning Electrochemical Microscopy of Corrosion of Si-containing Alloy in Chloride ions-Containing Acid

Corrosion behavior of Fe–3 at.% Si alloy in 0.01 mol dm^{-3} HCl solution was investigated by using scanning electrochemical microscopy (SECM) as well as general electrochemistry. The rate of corrosion coupled with hydrogen evolution was initially 0.44 A m^{-2} but decreased significantly with time. Localized hydrogen evolution on the specimen surface was probed by an SECM system in which a force sensor was mounted to determine the probe height from the specimen surface. SECM images revealed that hydrogen evolution took place heterogeneously on the specimen surface depending on crystallographic orientation of substrate single grains in the initial stage and then became relatively homogeneous. Finally, a heterogeneous hydrogen distribution corresponding to the appearance of localized corrosion sites was observed.

Other Activities

In May, Prof. H. Habazaki and Mr. T. Tanvir participated in the 2007 International Conference on Advanced Capacitors (ICAC2007), Kyoto and presented the papers entitled “Electrochemical Capacitance of Novel Brush-type Nanocarbons Prepared by a Template Method” and “Novel Approach for the Processing of Niobium Electrolytic Capacitors”, respectively. In this conference Mr. Tanvir won a student poster award. In September, Dr. K. Fushimi participated in the EuroCorr 2007, Freiburg, Germany and the 12th European Conference on Applications of Surface and Interface Analysis (ECASIA’07), Brussels, Belgium to present the papers entitled “Repassivation Current Transient from Iron Surface during Downward Micro-indentation in pH 8.4 Borate Solution” and “Depth Profiling Analyses of the Anodic Films and Passive Films by Glow Discharge Optical Emission Spectroscopy”, respectively. Prof. H. Habazaki was invited in E-MRS Fall Meeting 2007, Warsaw, Poland and presented the paper “Structural Control of Anodic Titanium Oxide Using Non-equilibrium Titanium Alloys”. In October, Prof. Emeri. M. Seo was invited in the 212 th ECS Meeting, Washington DC, USA and presented the paper “ Changes in Surface Stress of Au Electrode during Underpotential Deposition of Bi and Pb”. In November, Prof. H. Habazaki was also invited in the 1st Korea-Japan Joint Conference of Anodizing Research Society, Jeju, Korea to present the paper “Field Crystallization of Anodic Oxides – its Mechanism and Suppression”.

Presentation

T. Tanvir, K. Fushimi, H. Habazaki; Novel Approach for the Processing of Niobium Electrolytic Capacitors, 2007 International Conference on Advanced Capacitors, (ICAC2007), 2007.5.28-30, Kyoto, Japan (2007).
M. Kiriu, K. Fushimi, H. Konno, H. Habazaki; Electrochemical Capacitance of Novel Brush-type Nanocarbons Prepared by a Template Method, ibid.

T. Nakayama, M. Sakairi, K. Fushimi, S. Hashizume; Investigations on the local electrochemical behavior of welded stainless steels with solution flow type micro-droplet cell, EuroCorr 2007, 2007.9.9-13, Freiburg, Germany (2007).

K. Fushimi, T. Yamamoto, M. Seo, H. Habazaki; Repassivation Current Transient from Iron Surface during Downward Micro-indentation in pH 8.4 Borate Solution, ibid.

H. Habazaki, M. Uemura, K. Fushimi, K. Shimizu, S. Nagata, P. Skeldon, G.E. Thompson; Depth profiling analyses of the anodic films and passive films by glow discharge optical emission spectroscopy, 12th European Conference on Applications of Surface and Interface Analysis (ECASIA’07), 2007.9.9-14, Brussels, Bergium (2007).

T. Nakamura, K. Azumi, K. Fushimi, H. Konno; Measurement of pH distribution in PEFC using small glass electrodes, 58th Annual Meeting of the International Society of Electrochemistry, 2007.9.9-14, Banff, Canada.

A. Naganuma, K. Azumi, K. Fushimi, H. Habazaki; Development of multi-channel electrode method and its application to crevice corrosion, ibid.

A.W. Hassel, K.A. Lill, R. Rablbauer, M. Stratmann, K. Fushimi, M. Seo; Corrosion and passivity of FeAlCr light weight steels, ibid.

H. Habazaki, M. T. Tanvir, Y. Oikawa, K. Fushimi; Structural control of anodic titanium oxide using non-equilibrium titanium alloys, E-MRS Fall Meeting 2007, 2007. 9.17-21, Warsaw, Poland (2007).

M. Seo, M. Yamazaki; Changes in Surface Stress of Au Electrode during Underpotential Deposition of Bi and Pb, 212 th ECS Meeting, 2007. 10. 7-12, Washington DC, USA (2007).

H. Habazaki, K. Shimizu; Field crystallization of anodic oxides – its mechanism and suppression, 1st Korea-Japan Joint Conference of Anodizing Research Society, 2007.11.2-3, Jeju, Korea (2007).

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Y. Hara, K. Saito, R. Goto. M. Kinjo, K. Yanada, Y. Wachi

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) Formation of nano-rods of aluminum hydroxides by using porous anodic oxide film on aluminum as a template and source materials

Aluminum specimens covered with porous anodic oxide films were immersed in boiling distilled water. During the immersion, aluminum oxide reacts with hot water to form rods of crystalline hydroxides, pseudo-boehmite, in the pores. After hydroxide rod formation, the specimens were immersed in saturated $SnCl_4$ solution and then in sodium citrate solutions to remove the metal substrate and aluminum oxides. Finally, nano rods of pseudo-boehmite were exposed. The length and width of nano-rods were controlled by changing the anodizing condition.

(3) Formation of Al-Nb composite oxide films on aluminum by liquid phase

deposition and anodizing

Electropolished and DC-etched aluminum specimens were coated with Nb_2O_5 films by a liquid phase deposition method, where the specimen covered with crystalline anodic oxide films was immersed in solutions containing Nb-fluoride and borate ions. After depositing Nb_2O_5 films, the specimen was anodized to form Al-Nb composite oxide films. The composite oxide film on both types of specimens showed larger capacitances than aluminum anodic oxide films, and this trend was more remarkable on DC-etched specimens.

(4) 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 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.

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

Platinum electroplating under galvanostatic conditions with different current densities was attempted on copper specimens in a $Pt(NH_3)_2(NO_2)_2$ / CH_3COONa / Na_2CO_3 solution to examine the mechanism for the crack formation in platinum layers, using a stress / strain gauge. A tensile force increased rapidly at the initial stage of electro-plating, and, through a sharp peak, decreased to reach a steady value at each current density, and the rate of increase in the tensile stress increased with increasing current density. Crack formation was found to start just before the peak of tensile stress, suggesting that the measurement of stress using the stress / strain gauge is useful for the evaluation of crack formation in Pt-layers.

(6) Study on corrosion of HAZ of anti-corrosion line pipe by electrochemical micro droplet cell

Solution flow type droplet cell was applied to investigate the influences of oxidized scales, PWHT and stress on corrosion behaviors of HAZ of corrosion resistant line pipes. The closer a part of the as-welded surface is to the weld boundary, the lower its corrosion potential is. The higher stress on the specimen is, the lower its corrosion resistance becomes. The corrosion resistance of HAZ could be significantly improved by removing the oxidized scale on its surface.

(7) Nickel/Copper deposition on aluminum covered with porous anodic oxide films

This investigation is related to the development of new types of gravure printing roll, which can be used repeatedly. Aluminum specimens were anodized in an oxalic acid solution to form porous anodic oxide films on the specimen, and Ni-P / Cu layers were deposited by electroless-/elector-plating after Pd seeding treatments. Detachment tests showed that Ni-P / Cu layers can be detached at the interface between anodic oxide film and Ni-P layer by relatively weak mechanical force.

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

In a previous investigation, poly-pyrrole deposited on an Au layer, which had been electroplated on aluminum, lost an electro-conductivity by dissolving the aluminum substrate in NaOH solution on open circuit, while the aluminum dissolution by connecting Pt plate prevented the poly-pyrrole from the loss of conductivity. This investigation was carried out to establish the mechanism of change in the conductivity, and involves the monitoring of current between the specimen and Pt plate and of rest potential. The current between the specimen and Pt plate showed a steady value during immersion and the rest potential was higher in the case of Pt-connection that simple immersion. The prevention of electro-conductivity loss of poly-pyrrole was explained in terms of the preferential galvanic corrosion of the aluminum substrate at higher potentials.

(9) Corrosion of aluminum alloys in alcohols at high temperature

Corrosion of aluminum alloys containing Sn and Bi in main component alcohols of brake fluid was investigated. No. 1000 aluminum alloys corroded by immersing in 2-(2-(2-methoxyethoxy) ethoxy)ethanol (MEEE) and 2-(2-(2-butoxyethoxy)ethoxy)ethanol (BEEE) at 415 K for 24 h. MEEE was more aggressive than BEEE in the corrosion of aluminum alloys at 415K. Copper phase was adjacent to Sn in 2000 aluminum alloys, and Mg formed intermetallic compounds with Sn in 6000 alloys. This causes the suppression of corrosion-enhancing effect with Sn in 2000 and 6000 aluminum alloys.

(10) Effect of Cu^{2+} and Mg^{2+} ions on corrosion behavior of aluminum in dilute chloride ion solution

In dilute chloride ion solution such as tap water or river water, corrosion usually does not occur. However, sometimes corrosion was observed. Last year, we studied influence of Cl^- ion concentration on corrosion by polarization tests and galvanic corrosion tests. This year, we examined synergy effect of Cu^{2+} and Mg^{2+} ions on corrosion behavior of aluminum in dilute chloride ion solution. If Cu2+ ions exist in the solution at very low concentration, Cu was deposited on aluminum surface by cathodic reaction while immersion corrosion test. Addition of cation, rest potential changes to positive direction, and localized corrosion occurs during galvanic corrosion test. If it absence of Cl^- ion in solutions containing Cu^{2+}, localized corrosion could not observed even if the same concentration of pitting corrosions were observed.

(11) Formation of model edge face by laser fabrication and Corrosion behavior of model edge face

An edge face of coated steels is a weak area for corrosion. From now on, Cr conversion treatment inhibit corrosion problem at the edge face. In near future, it could not use Cr conversion treatment or Cr^{6+} related surface treatments. The corrosion mechanism of edge face of Cr^{6+} surface treatment free coated steels. We applied laser fabrication technique on this type of corrosion study. The laser fabrication technique makes it possible to form model edge face on painted Zn coating steel. The rest potentials did not change with area ratio of Zn coating and steel substrate, because of very high Zn dissolution rate. However, an amount of corrosion products measured after longer immersion tests becomes lager with the area ratio.

(12) Crack formation in porous anodic oxide films on aluminum by heating

Pure aluminum specimens were anodized in 15 %-H_2SO_4 solution at different current densities at 293 K to form porous type anodic oxide films, whose thickness was adjusted to almost 15 μm by controlling anodizing time. Some of anodized specimens were immersed in boiling distilled water for 15 min to seal pores. Crack formation in the anodic oxide film was pronounced as heating temperature is raised below 673 K, while, above 77 K, cracks were not formed, but concaves were formed along the grain boundary of the substrate. Anodic oxide films after pore-sealing showed easier cracking at lower temperatures, suggesting the brittle properties of crystalline hydroxides.

(13) Fabrication of Cu micro-pattern on organic resin board by electroless plating and laser irradiation.

A printed circuit board with a fine Cu pattern was fabricated by electroless plating and laser irradiation. An epoxy resin plate was immersed in a Pd ion solution, and a Cu layer was then deposited on the resin by Cu electroless plating. After Cu plating, the Cu deposited specimen was irradiated with a YAG laser to remove the Cu layer locally. Fine Cu-pattern coils with 60 µm width and 20 µm intervals were fabricated on the epoxy resin by laser irradiation in air.

(14) Anodic reaction of titanium in vitro.

Initial surface condition is very important for not only corrosion but also other electrode reactions. Therefore, electrochemical polishing was applied to form the surface. The electrolyte for titanium electrochemical polishing is usually used harsh chemicals and operating temperature usually very low. We have changed the electrolyte from H_2SO_4 ethanol solution to NaCl ethylene glycol solution. We have examined optical electrochemical polishing conditions. The repassibation kinetics of titanium, which was electrochemical polished in new electrolyte and anodized, was examined in Hanks and PBS by PRM (photon rupture method). In the experimental conditions, titanium was repassivated after oxide films were removed by PRM. Every applied potential, the current after removed anodic oxide film in Hanks is lager than that in PBS.

(15) Formation of microstructure with solution flow type micro droplet cell

The flow type of micro droplet cell was applied to form high aspect ratio 3D microstructures on cupper substrate. This technique makes it possible to fabricate Ni and Cu micro rods that width about 100 μm and aspect ratio is more than 100. To change the solution during deposition, Ni/Cu/Ni layered micro rods also can form. To control the moving of the droplet, T and L shaped micro-rods can formed.

(16) Anodic reaction of aluminum alloy in shape controlled micro-pit

Corrosion type of aluminum and its alloys is mainly pitting corrosion, therefore corrosion reaction in shape controlled micro pits are very important to understand influence of aspect ratio on corrosion. Laser micro fabrication (Photon rupture method) and anodizing techniques applied to form shape controlled micro-pit on aluminum and also examined the influence of shape on localized corrosion behavior of aluminum. To control laser irradiation time makes it possible to fabricate artificial micro-pits with different aspect ratio. To use aperture makes it possible to activate only bottom of micro-pit. Aspect ratio affects on repassivation kinetics in artificial pits.

(17) Effect of initial surface on aluminum anodic oxide film structure by Spring 8

facility

Anodic oxide film structure formed on aluminum strongly affect by initial surface condition such as polishing way and keeping condition after the polishing. An air formed film, which prepared different polishing and preservation conditions, and anodic oxide film structures were analyzed by X-ray diffraction of Spring 8 facility. From diffraction results, it strongly suggests that degree of crystallinity of air formed oxide correlated with degree of crystallinity of anodic oxide film. This results also good relation with anodizing behavior.

Other activities

In May, Assoc. Prof. Sakairi attended International Corrosion Engineering, Conference in Seoul, Korea to present a paper entitled " Electrochemical Random Signal Analysis During Localized Corrosion of Anodized 1100 Aluminum Alloy in Chloride Environments".

In September, Assoc. Prof. Sakairi and Mr. T. Nakayama attended Eurocorr 2007 in Konzerthaus Freiburg im Breisgau, Germany. Mr. Nakayama presents a paper entitled "Investigations on the local electrochemical behavior of welded stainless steels with solution flow type micro-droplet cell", and Assoc. Prof. Sakairi presents a paper entitled " Electrochemical random signal analysis on galvanic corrosion of anodized aluminum alloy in chloride environments".

In October, Prof. Takahashi, Dr. Kikuchi, and Mr. Jha attended the 212nd ECS meeting at Washington D. C. and presented papers entitled “Deposition of Copper on Aluminum Covered with Anodic Oxide Films by Laser Irradiation and Electroplating” (Takahashi), “Three-Dimensional Micro-Actuator Fabrication by Aluminum Anodizing, Laser Irradiation, and Electrodeposition”(Kikuchi), and “Metallic Micropatterns on Anodic Alumina: Laser-Assisted Exposure of Trapped Seeds for Metallization”(Jha).

In November, Prof. Takahashi, Mr. Nagahara attended the 24th ARS Conference at Jeju Island, Korea, and presented paper entitled “Anodic Alumina:

Towards Micro and Nano-Technology", "Study on the Formation of Porous Anodic Oxide Films on Aluminum by Scanning Confocal Laser Microscopy". Assoc Prof. Sakairi attended Galvatech 2007 in Osaka, Japan to present a paper entitled "Improving Of Protection Of Zinc-Aluminum Alloy Coated Steels Against Corrosion by Anodizing".

Presentations

Effect of HAP coating on initial stage of repassivation of Ti; M. Sakairi, H. Miyata and H. Takahashi: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, Jan., 2007.

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Improvement of corrosion resistance coated steels by anodizing; M. Sakairi, A. Kageyama, Y. Uchida and H. Takahashi: Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Asahikawa, July, 2007.

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Effect of pit structure on localized corrosion of Al; A. Kageyama, M. Sakairi and Y. Kojima: ibid.

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LABORATORY OF HIGH TEMPERATURE MATERIALS

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Research work at "Laboratory of high temperature materials" directs toward 1) high-temperature corrosion of Cr-Si-Ni alloys, 2) high-temperature oxidation of metal disilicides in H_2O-containing atmosphere, 3) microstructures of oxidation scales formed on NiAl-X alloys, 4) development of advanced high-temperature materials of Nb-Si-B system, 5) structures of oxide scales formed on carbon steels, stainless 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) High-temperature corrosion behavior of Cr-Si-Ni alloys
High-temperature corrosion tests of Cr-Si-Ni alloys are being done. The Cr-Si-Ni alloys have good corrosion resistance to all aggressive salts, comparing with Ni-50Cr alloy. This result suggests that the SiO_2/Cr_2O_3 double layer scale is very effective for preventing sulfidation and chlorination of alloys.

(2) Oxidation behavior of metal disilicides in H_2O-containing atmospheres
In order to clarify the effects of B addition on the formation of protective oxide scales on B added disilicides in H_2O-containing atmosphere, evaporation behavior of B-SiO_2 was examined. The results demonstrated that the addition of B to SiO_2 led to the formation of borosilicate and the suppression of evaporation of SiO_2. In addition, the addition of B led to improvement of plasticity of SiO_2 (prevention of cracking).

(3) Microstructures of oxide scales formed on NiAl-X alloys
In order to clarify the microstructures of oxide scales formed on NiAl or NiAl-X alloys, the oxidation tests in H_2O-containing atmosphere have been done. Microstructures of oxide scales formed on NiAl or NiAl-X alloys are being observed by TEM. The oxide scale formed on NiAl-Cr in H_2O-containing atmosphere consisted of duplex layer: an outer scale consisting of equiaxed Al_2O_3 grains and an inner scale columnar Al_2O_3 grains. The oxide scale formed on NiAl-Cr-Zr in H_2O-containing atmosphere consisted of bigger columnar Al_2O_3 grains in size. These results suggested that the formation of oxide scale consisting of columnar Al_2O_3 was caused by inward diffusion of oxidant.

(4) Development of advanced high-temperature materials of Nb-Si-B system
Nb/$NbSi_2$ and Nb/B-$NbSi_2$ diffusion couples are heated up to 1573-1773K, and kept for up to 4 hours. Interface reaction layers formed during annealing were

analyzed by using SEM and EPMA. A Nb_5Si_3 layer was formed at the interface of Nb and $NbSi_2$ by preferential diffusion of Si from $NbSi_2$ to Nb. The reaction layer grew parallel to the interface. On the other hand, $Nb_5(Si,B)_3$ formed at the interface of Nb and B-$NbSi_2$ grew with irregularity. B diffuses through the $Nb_5(Si,B)_3$ layer and concentrates at the Nb/$Nb_5(Si,B)_3$ interface. This enrichment of B plays a role as a diffusion barrier for Si diffusion from B-$NbSi_2$ to Nb.

(5) High-temperature oxidation of carbon steels, stainless steels and aluminum alloys in H_2O-containing atmospheres
In order to clarify the microstructures of oxide scales formed on Al-Mg alloys with various Mg concentrations, oxidation tests are being done in H_2O-containing atmospheres. The thickness of oxide scale (mainly MgO scale) increased as the Mg concentration in the alloys and water vapor concentration in the atmospheres increase. The research on the effect of Mg concentration on the mechanical properties of oxide scales is also in progress. Similarly, oxidation behavior and scale structures of carbon steels and stainless steels in H_2O-containing atmospheres are also being investigated.

(6) Corrosion behavior of iron-based alloys in molten lead-free solders
The research on corrosion of iron-based alloys in molten lead-free solders such as Sn-Ag-Cu and Sn-Ag-Al is in progress. The concentrations of Cr and C and the structures of alloys strongly affected the corrosion behavior of the iron-based alloys. In addition, effects of alloying constituents on the microstructures of solidified lead-free solders are also studied.

In May, Prof. Kurokawa and Dr. Yamauchi attended The 6th Pacific Symposium on Flow Visualization and Image Processing held in Hawaii, and presented papers entitled “Surface Oxidation and Morphology Change of Rapidly Quenched FeAl Single Crystal”. In June, Prof. Kurokawa visited the Dong-Eui University in Busan, Korea, to establish the agreement to promote educational and academic exchanges and cooperation between the university and our research center. In September, Prof. Kurokawa attended The 6th International Symposium on Applied Science held in Nikko and also presented a paper entitled “Interfacial Reactions between Nb and $NbSi_2$ or $NbSi_2$-B”. In October, Prof. Kurokawa attended The 5th Inter’l Conf. on Physical and Numerical Simulation of Materials Processing held in Zhengzhou, China, and presented a paper entitled “Numerical Simulation of Solidified Structure Formation of Al-Si alloy Casting Using Cellular Automaton Method”.

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
SEM
Micro Vickers Hardness Tester
Acoustic Emission

Presentations

Effect of Zr Addition on Structure of Substrate/Oxide Scale Interface Formed on NiAl-based Alloy; H. Tomoto, S. Kawata, A. Yamauchi, S. Watanabe, K. Kurokawa and T. Narita: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Muroran, Jan., 2007.

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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-1□, IL-8, TNF-□, M-CSF and implantation test in soft tissue was done and bioreaction was evaluated. With the decrease of particle size the cytotoxicity originated from the physical size effect was pronounced especially below 10□m. 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 $CaO\text{-}P_2O_5\text{-}SiO_2\text{-}Al_2O_3$ (CPSA) glass fibers of 8-20μm in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bis-GMA. The improvement has been done to obtain the adequate flexural strength and higher torque. FRP wire shows the sufficient flexural strength and a very good elastic recovery. The dependence of Young's modulus and flexural stress on fiber fraction obeys very well the rule of mixture. This FRP wire can cover the range of the strength corresponding to the conventional metal orthodontic wires from Ni-Ti used in the initial stage of orthodontic treatments to Co-Cr used in the last stage by changing the volume ratio of glass fibers with the same external diameter. FRP wire can satisfy both mechanical properties and estheticity, which is not possible for the conventional metal wire.

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

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

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

The in vitro cell functional tests on cell 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-□, 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-□ was found only in the 1-3□m Ti particle mixed Hank's solution, which suggests that particles were phagocytized. SEM observation and EDS elemental analysis confirmed the phagocytosis of Ti particles by neutrophils.

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

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

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

Composite resin with fillers of ceramic powders in polymer matrix has estheticity similar to natural teeth color and is widely used for treatments of caries in incisal teeth. Physical-mechanical anchoring effect plays an important part in binding force between teeth and composite resin. The pretreatment to make etching of teeth is generally done using acid agents for enhancement of binding. SEM is usually used for the evaluation of etching effect. It can observe, however, only the result after a certain etching time. To observe the sequence of etching process it is necessary to prepare the series of specimens treated with different etching time. Atomic force microscope is applied for the in-situ observation of etching process of human enamel and dentin in acid agents. The chronological change of surface morphology can be successively observed and quantitative analysis is done for different etching conditions.

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

Laser lithography, one of the CAD/CAM systems to fabricate the polymer models by piling up the thin slices, which are photo-polymerized by scanning laser beam originally on the shallow depth of liquid epoxy monomer, was applied for the fabrication of dental 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 2μm thickness is coherent to matrix Ti and enough strong. Abraded volume by ultrasonic scaler was increased with the load in Ti, while no trace was formed in Ti-(N), instead stainless tip of scaler was abraded. The test showed that abrasion would be negligibly small under the practical conditions of the load 50g in clinics. Ti-(N) with biocompatibility and surface abrasion resistance would be suitable as abrasion-resistant implant materials for the application to the artificial joint of implant and 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.Xiaoming Li of Tsinghua University, Beijing, China joined to our laboratory on April 2007 as the postdoctoral researcher of the Japan Society for Promotion of Science (JSPS) for the development of nano-structured scaffold for medical and biochemical applications.

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

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).

Facilities and Capabilities

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

Presentations

Internal Diffusion of Micro/Nanoparticles Inside Body; F.Watari, S.Abe, K.Tamura, M.Uo, A.Yokoyama, Y.Totsuka:, The20th International Symposium on Ceramics in Medicine, Nante (France), Oct.24-7, 2007

Reaction of cell and tissue to material nanosizing; F.Watari, S.Abe, T.Akasaka, M.Uo, M.Matsuoka, N.Takashi, Y.Totsuka; 17th Iketani Conference The DOYAMA Symposium on Advanced Materials, Tokyo, Sept. 5-8, 2008

Internal Motion of Micro/Nano Particles of Titanium Oxides and Others in the Body; F.Watari, S.Abe, C.Koyama, A.Yokoyama, T.Akasaka, M.Uo, M.Matsuoka, Y.Totsuka, M.Esaki, M.Morita, T.Yonezawa, Asian BioCeramics Symposium 2007, Osaka, Sept. 25-7, 2007

High Resolution Observation of Carbon Nanotubes Implanted in Tissue by High Voltage Electron Microscopy; F.Watari, S.Abe, C.Koyama, S.Inoue, T.Akasaka, M.Uo, M.Matsuoka, N.Takashi, Y.Totsuka, E.Hirata, A.Yokoyama, M.Esaki, M.Morita, T.Yonezawa, International Dental Materiaks Congress (IDMC) 2007, Bangkok, Nov.21-4, 2007

Effect of nanosizing of materials on living organism; F.Watari, S.Abe, C.Koyama, S.Inoue, T.Akasaka, M.Uo, M.Matsuoka, N.Takashi, Y.Totsuka, E.Hirata, A.Yokoyama, M.Esaki, M.Morita, T.Yonezawa:, International Symposium on Nano Science and Technology (ISNST) 2007, Tainan, Nov. 8-9, 2007

The toxicity of nanomaterials and the dependency on their size and shape; F. Watari, The 127th meeting of Japan Phermaceutical Society, Toyama, Mar.28-30, 2007

XSAM observation of micro/nano particle distribution in inside body; F. Watari, S. Abe, N. Sakaguchi, A. Yokoyama, Y. Nodasaka, T. Akasaka, M. Uo, The 63th Annual Meeting of the Japanese Society of Microscopy, Niigata, May 20-22, 2007

Functional conversion of nano particles with biological process, F. Watari, A. Yokoyama, M. Gelinsky, S. Liao, S. Inoue, T. Akasaka, The 29th meeting of Japan Biomaterials Society, Toyonaka, Nov. 26-7, 2007

Chemical state analysis of titanium and nickel in the surrounding tissues of metallic implants; M. Uo, K. Asakura, F. Watari, , 9th International Conference on Biology and Synchrotron Radiation, Manchester, Aug, 2007

M.Uo, T.Akasaka, S.Abe, F.Watari: XAFS Analysis of Ti, Ni-Ti and SUS304 Implanted Rat Soft Tissues, Proc. International Dental Materiaks Congress (IDMC) 2007, 157, 2007

Preparation and properties of carbon nanotube membrane; M. Uo, S. Abe, T. Akasaka, F. Watari, The Japanese Society of Dental Materials and Devices, Sapporo, May 12-13, 2007

The study of dissolution property of TI, Ni-Ti alloy and SUS304 using fluorescence XAFS method; M. Uo, K. Asakura, F. Watari, The 10th XAFS conference, Sapporo, July 25-7, 2007

Inhibition of growth of *Streptococcus mutans* by artificial glyco-polymer; T.Akasaka, S.Abe, M.Uo, F.Watari; the 19th Congress of Society for Organ Substitution and Regenerative Medicine, Sapporo, Feb. 2007.

Inhibition mechanism of growth of *Streptococcus mutans* with artificial glyco-polymer; T.Akasaka, S.Abe, M.Uo, F.Watari; the 49th General Session of the Japanese Society for Dental Materials and Devices, Sapporo, May. 2007.

Modification of carbon nanotubes with apatite; T.Akasaka, S.Abe, M.Uo, F.Watari; the 17th Inorganic Phosphorus Chemistry Symposium, Sapporo, Oct. 2007.

Inhibition of growth of *Streptococcus mutans* by artificial glyco-polymer; T.Akasaka, S.Abe, M.Uo, F.Watari; International Dental Materials Congress 2007, Bangkok, Thailand, Nov. 2007.

Distribution of nano materials in mice using a scanning X-ray analytical microscopy, Shigeaki ABE, Chika KOYAMA, Tsukasa AKASAKA, Motohiro UO, Yoshinori KUBOKI, Fumio WATARI, Joint Meeting of the Iron and Steel Society and the Japan Institute of Metals, Hokkaido Division, Sapporo, Feb. 6, 2007.

Photodissociation mechanism of ozone-water complex in troposphere. Shigeaki ABE, Fumio WATARI, Hiroto TACHIKAWA, Winter meeting of the Chemical Society of Japan, Hokkaido Division, Sapporo, Feb. 6-7, 2007

Observation of several inorganic particles in mice, Shigeaki ABE, Tsukasa AKASAKA, Motohiro UO, Yoshinori KUBOKI, Fumio WATARI, The Japanese Society of Dental Materials and Devices, Sapporo, May 12-13, 2007

Visualization of Distribution of Inorganic Micro/Nano Particles in Mice Using X-ray Scanning Electronic Microscope, Shigeaki ABE, Chika KOYAMA, Tsukasa AKASAKA, Motohiro UO, Yoshinori KUBOKI, Fumio WATARI, International Dental Materials Congress 2007, Bangkok, Nov. 21-24, 2007

Determination of Administered Magnetite Nanoparticles in Mice: Magnetic Resonance Imaging and X-ray Scanning Electronic Microscope. Mitsue ESAKI, Shigeaki ABE, Ikuhiro KIDA, Tsukasa AKASAKA, Motohiro UO, Yoshinori KUBOKI, Fumio WATARI, International Dental Materials Congress 2007, Bangkok, Nov. 21-24, 2007

Inhibition of Growth of Streptococcus Mutans by Artificial Glycol-polymer, Tsukasa AKASAKA, Shigeaki ABE, Motohiro UO, Fumio WATARI, International Dental Materials Congress 2007, Bangkok, Nov. 21-24, 2007

XAFS analysis of Ti, Ni-Ti and SUS304 implanted rat soft tissues, Motohiro UO, Tsukasa AKASAKA, Shigeaki ABE, Fumio WATARI, International Dental Materials Congress 2007, Bangkok, Nov. 21-24, 2007

Visualization of biodistibution of organic/inorganic particles in mice, Shigeaki ABE, Chika KOYAMA, Iosif Danel Rosca, Tsukasa AKASAKA, Motohiro UO, Yoshinori KUBOKI, Fumio WATARI, Annual meeting of Biomaterial Society of Japan, Suita, Nov. 26-27, 2007

Influence of Microstructures on Bone-Related Cells, X. Li, F. Watari, K. de Groot, C. A. van Blitterswijk, H. Yuan. 1st Asian Biomaterials Congress. Fukuoka, Dec. 2007

New geometrical matrix for bone regeneration: A honeycomb-shaped β-TCP induced straight longitudinal bone inside the tunnel; M. TERADA, M. TAKAYAMA, N. NOMURA, M. SUZUKI, M. KOUNO, S. IKU, Y. ASO, T. KAKU, M.ISHIKAWA, Y. KITAGAWA. M. UO, F. WATARI, Y. KUBOKI; 19th Society for Organ Substitution and Regenerative Medicine, Sapporo, Feb.2, 2007

New geometrical matrix for bone regeneration: A honeycomb-shaped β-TCP induced straight longitudinal bone inside the tunnel; Y. KUBOKI, M. TERADA, M. TAKAYAMA, M. KOUNO, S. IKU, Y. ASO, T. KAKU, Y. KITAGAWA. M. UO, F. WATARI; The 39th Japanese Society for Connective Tissue Research & The 54th annual meeting of the Jaoan Matrix Club, Tokyo, May9-11 2007

Development of multi walled carbon nanotubes coated collagen for cell culturing; M. TERADA, M. UO, Y. KUBOKI Y. KITAGAWA. F. WATARI; The 49th General Session ofthe Japanese Society for Dental Materials and Devices, Sapporo, May12-15 2007

Triple-helix structure of collagen is essential for its interaction with carbon nanotubes; Y. KUBOKI, M. TERADA, Y. KITAGAWA, M. UO, F. WATARI; 49th Japanese Association for Oral Biology, Sapporo, Aug.29-31, 2007

Biocompatibility of Carbon Nanosubstances in the Subcutaneous Tissue; Eri Hirata, Atsuro Yokoyama, Yoshinori Sato, Yoshinobu Nodasaka, Motohiro Uo, Tsukasa Akasaka, Kazuyuki Tohji, Fumio Watari : The 33rd Fullerene-Nanotubes General Symposium, July 2007

LABORATORY OF ADVANCED HIGH-TEMPERATUER MATERIALS

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The research activities of the laboratory are directed toward study and development of the advanced high strengthened ODS alloys and high temperature corrosion, oxidation and protection of metals.

(1) Nano-meso structure control of 9Cr-ODS ferritic steels

Structure of the 9Cr-ODS ferritic steels can be successfully controlled by the $\alpha-\gamma$ phase transformation, and their high-temperature creep strength is the most superior worldwide in the class of ferritic tubes. This is owing to existence of the residual ferrite phase within the tempered martensite phase. In our group, the formation mechanism of the residual ferrite and the origins its strength are intensively investigated through synthesizing ODS alloys by ball-milling and their analyses by means of nano-indentation measurement, differential thermal analysis, high-temperature X-ray diffraction, SEM and TEM observation.

It was clearly revealed that the ferrite is able to remain over Ac3 point by pinning of the $\alpha-\gamma$ interface due to nano-size oxide particles; this ferrite is a non-equilibrium phase, and designated as residual ferrite. This phase is composed of so-called ultrafine grains with size of 500 nm. Therefore, grain refinement strengthening can be effectively performed in the residual ferrite phase, which is the real origin for the superior high-temperature strength of the 9Cr-ODS ferritic steels.

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

The appropriate cold-rolling and heat-treatment processes are being investigated for the manufacture of 12Cr-ODS ferritic steels, focusing on the texture development. A measurement technique by FE-SEM/EBSP (Electron Back Scattering Pattern) is mainly applied in this study. Cold-rolling of the sheet induces strong $\alpha-$fiber texturing composed of {111}～{001}<110> parallel to the rolling direction and rolling plane. Recrystallization of the cold-rolled sheet takes place at elevated temperatures beyond 1100℃. The formation mechanism of the recrystallized texture, typically {011}<001>, was investigated; this unique texture was revealed to exist within shear bands of the cold-rolled structure. This finding suggests that the recrystallized grains are nucleated during the stage of cold-rolling, and are selectively grown at temperatures beyond 1100℃.

(3) Development of Ni-based ODS superalloys

Basic study for development of the Ni based ODS superalloys is being conducted. It was found that mechanical alloying (MA) induces nano-crystal formation of in 50 nm size in the Ni-Y_2O_3 system, and the nano-size grains are maintained up to 1300℃. Beyond this temperature, recrystallization and grain-growth takes place due to coarsening of Y_2O_3 oxide particles. A study for making extremely fine distributions of oxide particles is being also conducted; the effective elements for fine oxide particle distribution were discovered and a patent application is in preparation. In addition, effects of MA on γ' (Ni_3Al) precipitation and growth in the Ni-Al-Y_2O_3 system and more practical alloys (MA6000) were investigated. MA induces a spherical shape of γ' precipitate, whilst conventional arc-melting forms cuboidal type. The dominant factor controlling shape of γ' precipitates was found to be the misfit parameter between γ' and the MA-matrix.

(4) Water vapor effects on the high temperature oxidation of Ni-based alloy

The effects of water vapor on the oxidation of Pt-modified γ'-Ni_3Al alloys are being investigated. Water vapor decreased the critical Al content for exclusive Al_2O_3 scale formation, even when Pt content was high, ~10at%. Oxide scales consisted of thick duplex outer NiO and inner $NiAl_2O_4$ + Pt(Ni) structure, however, the parabolic rate constant was lower than that in dry conditions. The study of pure-Ni oxidation in atmospheres containing water vapor indicated that a very fine powder of NiO was formed on the NiO scale surface, and it could detach from the surface causing weight loss during oxidation.

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

Studies into the effects of various elements on the phase transformation behavior of Al_2O_3 scale are being conducted. The reactive element of Hf was found to delay metastable to stable phase transformation of Al_2O_3 scale formed on Pt-modified γ'-Ni_3Al alloy. Large differences were observed in the α-Al_2O_3 scale microstructure due to the different heterogeneous nucleation and growth mechanisms of α-Al_2O_3 nuclei.

(6) Spallation and cracking behavior of Al_2O_3 scale during creep deformation

Creep deformation behavior of Al_2O_3 scale formed on an oxidation resistant coating on Hastelloy-X alloy was investigated. The Al_2O_3 scale was creep-deformed without cracking or spallation when the creep rate of the substrate was sufficiently slow. With increasing creep rate, cracks were initiated perpendicularly to the stress direction, and the interval between cracks decreased.

(7) Effects of impurity elements on the spallation behavior of low-C steel

Scale spallation behavior was investigated on the low-C hot rolled steels with different contents of S and Mn. Oxide scale was easily spalled off on the high S steels when the oxidation was conducted above 1000°C and the scale thickness exceeded 140μm. High S content was found at the scale/steel interface, and the eutectic structure was observed at the interface. Those results indicated that scale spallation was caused by the formation of liquid phase at the interface due to eutectic reaction between Fe-FeS at about 980°C.

Presentations

Softening characteristic of tempering resistance in 9Cr-ODS ferritic steels; N. Chikata, S. Hayashi, S. Ukai, Y. Kohno, S. Ohtsuka and T. Kaito: ISIJ and Jpn, Inst. Metals joint meeting, July. 2007.

High-temperature tensile properties and microstructure of Ni-based ODS superalloy (PM1000); T. Hoshino, S. Hayashi and S. Ukai: ISIJ and Jpn, Inst. Metals joint meeting, July. 2007.

Development of Fe-based and Ni-based ODS alloys; S. Ukai: Summer School on Advanced high-temperature materials and deformation mechanism, Jpn. Inst. Metals, August 2007.

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Treatment, October 2007.

The Oxidation Behavior of Fe-20at.%Cr-10at.%Al-3at.%X (X=Ti, Mn, Nb) Alloys at 900ºC; Y. Kitajima, S.Hayashi, T.Natita and S. Ukai : Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2007.

Interdiffusion Behavior of Ni-Cr-Al and β-NiAl with Diffusion Barrier Coating; K. Ohno, S.Hayashi, T.Natita and S. Ukai : Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2007.

Mechanical Property of Hastelloy-X with and without Oxidation Resistance Coating; S.Hayashi, M. Sakata and T. Narita : The 157th Symposium on Corrosion Engineering.

Phase Transformation of Al_2O_3 Scale formed on Ni-22Al-30Pt Alloy at High Temperatures; S.Hayashi, T.Natita, S. Ukai and B. Gleeson : Jpn, Inst. Metals, Mar. 2007.

The Creep Behavior of Hastelloy-X with Diffusion Barrier Coating; M. Sakata, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Mar. 2007.

The Effect of Additional Elements on the Microstructure of Al_2O_3 Scale on Fe-20at.Cr-10at.%Al-(0-3)at.%X (X=Ti, Mn, Nb) Alloys at High Temperatures; Y. Kitajima, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Mar. 2007.

The Effect of S and Mn Additions on the Scale Spallation of Low Carbon Steels; T. Sekimoto, S.Hayashi, S. Ukai and K. Honda : Jpn, Inst. Metals, Mar. 2007.

Interdiffusion Behavior of Ni-Cr-Al with Diffusion Barrier Coating / Ni-50Al alloy diffusion couples; K. Ohno, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Mar. 2007.

Alumina Scale Evolution on Pt-Modified Ni_3Al-Based Alloys With and Without Hf During Short Term Oxidation; S. Hayashi : International Conference on High Temperature Corrosion 2007, New London, U.S, July, 2007.

The effect of additional elements on oxide scale evolution of Fe-Cr-Al alloys at high temperatures; Y. Kitajima, S.Hayashi, T.Natita and S. Ukai : International Conference on High Temperature Corrosion 2007, New London, U.S, July, 2007.

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The Oxidation Behavior of Ni-based Alloys with Oxidation Resistance Coating using Burner test Rig; J. Aoyama, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Sep. 2007.

Effect of Water Vapor on the Scale Evolution of Low Carbon Steels at High Temperatures; T. Sekimoto, S.Hayashi, S. Ukai and K. Honda : Jpn, Inst. Metals, Sep. 2007.

Effect of Additional Elements on Interdiffusion Behavior of Ni-Cr-Al and Ni-50Al alloy with Diffusion Barrier Coating; K. Ohno, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Sep. 2007.

Cycric Oxidation Behavior of $\gamma+\gamma'$-Ni-Al-Pt Alloys in H_2O-Contaning Atmospheres; M. Auchi, S.Hayashi and S. Ukai : Jpn, Inst. Metals, Sep. 2007.

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 focusing on 1) elucidating of the interaction between various alloys (superalloys, Ni-based alloys and Fe-based alloys) and coatings, 2) understanding high temperature oxidation and corrosion behavior of alloys and coatings, 3) comprehending the influence of coatings on mechanical properties, 4) developing a novel diffusion barrier system to improve high temperature capabilities.
Furthermore we are aiming to transfer our research successes to the practical use, such as 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, W, Ni, Cr) as a diffusion barrier and an outer Ni-aluminide as Al reservoir, was formed on superalloys, Ni-based alloys and Fe-based alloys (e.g. TMS-138, Hastelloy X and SUS301). 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 whit diffusion barrier

Oxidation behavior of oxidation resistant coating with diffusion barrier was examined by oxidation testing carried out at temperature between 1323 and 1423K. It was found that σ-(Re, W, Ni, Cr) ac as a diffusion barrier fro both inward diffusion of Al and outward diffusion of alloying elements in the alloy substrate.

(3) Interdiffusion of Pt into superalloy

Interdiffusion of Pt into Ni-based superalloys was investigated. 5μm of Pt layer was electroplated on superalloy substrate then were then heat-treated at 1273K for up to 100h in vacuum. Samples were cross-sectioned and prepared for analysis using an Ar ion cross-polisher, and then imged by SEM or FIB. Cross-sections were chemically analyzed by 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 rapid growth of meta-stable alumina phases at 1073-1173K, a think layer of titanium was deposited on the NiAl alloy. Oxide surface morphology and XRD revealed that uncoated NiAl alloy formed needle-like gamma or theta alumina at 1173K, however, no indication of whiskers on the surface of Ti coated NiAl.

Presentations

Interdiffusion Behavior of Ni-Cr-Al and □-NiAl with Diffusion Barrier Coating; K.

Ohno, S.Hayashi, T.Natita and S. Ukai : Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2007.

Mechanical Property of Hastelloy-X with and without Oxidation Resistance Coating; S.Hayashi, M. Sakata and T. Narita : The 157th Symposium on Corrosion Engineering.

Phase Transformation of Al_2O_3 Scale formed on Ni-22Al-30Pt Alloy at High Temperatures; S.Hayashi, T.Natita, S. Ukai and B. Gleeson : Jpn, Inst. Metals, Mar. 2007.

The Creep Behavior of Hastelloy-X with Diffusion Barrier Coating; M. Sakata, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Mar. 2007.

The Effect of Additional Elements on the Microstructure of Al_2O_3 Scale on Fe-20at.Cr-10at.%Al-(0-3)at.%X (X=Ti, Mn, Nb) Alloys at High Temperatures; Y. Kitajima, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Mar. 2007.

Interdiffusion Behavior of Ni-Cr-Al with Diffusion Barrier Coating / Ni-50Al alloy diffusion couples; K. Ohno, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Mar. 2007.

Alumina Scale Evolution on Pt-Modified Ni3Al-Based Alloys With and Without Hf During Short Term Oxidation; S. Hayashi : International Conference on High Temperature Corrosion 2007, New London, U.S, July, 2007.

The effect of additional elements on oxide scale evolution of Fe-Cr-Al alloys at high temperatures; Y. Kitajima, S.Hayashi, T.Natita and S. Ukai : International Conference on High Temperature Corrosion 2007, New London, U.S, July, 2007.

The Effect of Ti Addition on Al_2O_3 Scale Evolution of Fe-20at.%Cr-10at.%Al Alloy at High Temperatures; Y. Kitajima, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Sep. 2007.

The Oxidation Behavior of Ni-based Alloys with Oxidation Resistance Coating using Burner test Rig; J. Aoyama, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Sep. 2007.

Effect of Additional Elements on Interdiffusion Behavior of Ni-Cr-Al and Ni-50Al alloy with Diffusion Barrier Coating; K. Ohno, S.Hayashi, T.Natita and S. Ukai : Jpn, Inst. Metals, Sep. 2007.

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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 Shinnosuke Egoshi, Toshiro Nakamura, Humiyasu Nishiyama, Arisa Sasaki, Jun Kanno

Presentations

K Azumi, K. Iokibe; Analysis of Edge Corrosion of Zinc-Plated Steel in Humid Atmospheric Corrosion using Multiple Electrode System, Galvatech'07, Nov.18-22, 2007, Osaka University

K. Azumi, K. Fushimi, and A. Naganuma; Application of multichannel electrode system to corrosion monitoring, The 54th Annual Meeting of Japan Society of Corrosion Engineering, Hiroshima, Oct., 2007
A. Naganuma, K. Fushimi, K. Azumi, H. Habazaki and H. Konno; Corrosion monitoring of crevice corrosion using multichannel electrode system, *ibid.*

K. Azumi, S. Egoshi, H. Fujieda and H Konno; Direct electroless Ni-P plating on ADC12 dicasting alloy, 58th ISE Meeting, Banff, Canada, Sept, 2007
Toshiro Nakamura, Kazuhisa Azumi, Koji Fushimi, Hidetaka Konno;

Measurement of pH distribution in PEFC using small glass electrodes, *ibid.*
Hassan Elsentriecy (Japan), Kazuhisa Azumi, Hidetaka Konno; Stannate chemical conversion coating on Mg alloy using potentiostatic polarization method, *ibid.*
Atsushi Naganuma (Japan), Naganuma Atsushi, Kazuhisa Azumi, Koji Fushimi, Hiroki Habazaki; Development of multi-channel electrode method and its application to crevice corrosion, *ibid.*

K. Iokibe, H. Tachikawa and K Azumi; DFT calculation of adsorption states of organic molecular on Zn surface, The 116th Annual Meeting of Surf. Finish. Soc. Jpn., Nagasaki, Sept., 2007.

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S. Egoshi, K. Azumi, H. Konno, S. Kawashima; Direct plating of electroless Ni-P deposition film on Al-Si alloys using Cu pretreatment, *ibid.*
K. Iokibe, H. Tachikawa, K. Azumi and Hi Konno; DFT calculation of surface diffusion energy of Zn adatom on Zn surface, *ibid.*
T. Nakamura, K. Fushimi, K. Azumi, and H. Konno; pH measurement in PEFC using glass electrode, *ibid.*
A. Naganuma, K. Fushimi, K. Azumi, and H. Habazaki; Transition of corrosion behavior inside crevice measured by using multichannel electrode system, *ibid.*
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S. Egoshi, K. Azumi and H. Konno; Direct plating to Al-Si alloys using Cu-pretreatment, *ibid.*

H. Fujieda, S. Egoshi, K. Azumi and H. Konno; Electroless Ni plating on die casting Al alloy, *ibid.*

F. Nishiyama, K. Azumi and H. Konno; Carbon coating on porous alumina film, *ibid.*

ABSTRACTS of PUBLICATIONS

Decrease of Mg content in Al-Mg alloy by composite oxide from used dry battery

Mikito Ueda, Haku Ryu, Toshiaki Ohstuka, and Hidenori Takahashi

J. Japan Inst. Metals, 71, 1046-1049 (2007)

A composite oxide produced from used dry battery was used to decrease Mg content in Al-Mg alloy at high temperature. The oxide was found to consist of $ZnMn_2O_4$, $ZnMnO_3$, and ZnO by XRD analysis. After a reaction between a pellet made from the oxide powder and the alloy in liquid at 973K for 2h, Mg content in the alloy decreased from 4.0 to 3.6 mass%. During the reaction, metallic Mg probably diffused into the pellet to form $MgMn_2O_4$ and then exchanged with Zn(II) in $ZnMn_2O_4$. (Japanese)

The effect of counter anions on corrosion resistance of steel covered by bi-layered polypyrrole film

Damian Kowalski, Mikito Ueda, and Toshiaki Ohtsuka

Corrosion Science, 49, 3442-3452 (2007)

The bi-layered polypyrrole (PPy) coatings were investigated for corrosion prevention of a carbon steel. The inner layer was doped with the Keggin structure anions of $PMo_{12}O_{40}^{3-}$ (PMo_{12}) and HPO_4^{2-} anions for stabilization of the passive oxide film at the metal–polymer interface, and the outer layer was doped with four organic anions of dihydroxynaphthalenedisulfonate (DHNDS), naphthalenedisulfonate (NDS), anthraquinonedisulfonate (AnqDS) or dodecylsulfate (DoS) for inhibition of the decomposition and release of PMo_{12}. The corrosion tests were performed in 3.5 wt.% NaCl aqueous solution. The corrosion resistance of the steels covered by the bi-layered PPy films was found in the following order: PPy–PMo_{12}/PPy–DHNDS < PPy–PMo_{12}/PPy–NDS < PPy–PMo_{12}/AnqDS < PPy–P Mo_{12}/PPy–DoS. The performance of corrosion protection related to the oxidized state of the polymer was discussed.

The effect of ultrasonic irradiation during electropolymerization of polypyrrole on corrosion prevention of the coated steel

Damian Kowalski, Mikito Ueda, and Toshiaki Ohtsuka

Corrosion Science , 50, 286-291(2007)

Ultrasonic irradiation was imposed during electropolymerization of polypyrrole (PPy) in acid phosphate solution containing molybdophosphate ($PMo_{12}O_{40}^{3-}$) ions and pyrrole monomer. Corrosion of the steel coated by the PPy film prepared under ultrasonic irradiation was tested in 3.5 wt.% NaCl solution and compared with corrosion of the steel coated by the PPy film without ultrasonic irradiation. The PPy film prepared under ultrasonic irradiation kept the steel in the passive state one and a half times as long as that prepared without ultrasonic irradiation. Imposition of ultrasound enhanced the doping of $PMo_{12}O_{40}^{3-}$ and decreased the doping of HPO_4^{2-}. The surface morphology of the PPy film was changed with imposition of ultrasound in electropolymerization process. Under imposition of ultrasound, a dense and compact PPy layer was formed. The structure of the PPy film obtained under ultrasonic irradiation was assumed to result from change in nucleation-growth mechanism.

Corrosion protection of steel by bi-layered polypyrrole doped with molybdophosphate and naphthalenedisulfonate anions

Damian Kowalski, Mikito Ueda, and Toshiaki Ohtsuka

Corrosion Science, 49, 1635-1644(2007)

Bi-layered polypyrrole (PPy) coating was investigated for corrosion prevention of steels. The PPy coating consisted of the inner layer doped with $PMo_{12}O_{40}^{3-}$ (PMo_{12}) and HPO_4^{2-} ions and the outer layer doped with naphthalenedisulfonate (NDS) ions. PMo_{12} ions doped in the inner layer make the passive oxide film on steel stabilized and the outer layer doped with large organic ions of NDS restricts decomposition and release of PMo_{12} ions in the inner layer. Corrosion tests were made in 3.5% NaCl aqueous solution for the steels covered by the single PPy–PMo_{12}, single PPy–NDS, and bi-layered PPy–PMo_{12}/PPy–NDS coatings. The single PPy–PMo_{12} and PPy–NDS coatings maintained the steel in passive state for 34 h and 24 h, respectively. The bi-layered coating kept the steel in passive state and prevented corrosion of the steels for the longer time period.

An EQCM study of the deposition and doping/dedoping behavior of polypyrrole from phosphoric acid solutions

Silvio Koehler, Mikito Ueda, Igor Efimov, and Andreas Bund

Electrochimica Acta, 52, 3040-3046, 2007

The potentiostatic deposition of polypyrrole (PPy) from 0.1 M aqueous phosphoric acid solution and the doping/dedoping behavior of the resulting films have been investigated by the electrochemical quartz crystal microbalance (EQCM) technique. The change of the complex shear modulus during the film growth and during the doping/dedoping were calculated using the acoustic impedance method. It was found that the films contain only ca. 1 wt% water in the oxidized state which is in accordance with their relatively high storage modulus of 38 MPa and low loss tangent of 0.05. Comparing H_3PO_4 (pH 1) and NaH_2PO_4 (pH 8) it was found that the doping/dedoping in the latter is accompanied by a strong increase of the surface roughness which is a direct result of cation exchange present at pH 8.

Co-deposition of Al–Cr–Ni alloys using constant potential and potential pulse techniques in $AlCl_3$–NaCl–KCl molten salt

Mikito Ueda , Hirokuni Kigawa and Toshiaki Ohtsuka

Electrochimica Acta, 52, 2515-2519(2007)

To improve the oxidation resistance of TiAl intermetallic compound under high temperature condition, cathodic co-deposition of Al–Cr and Al–Ni alloy was carried out by constant potential control or potential pulse control in $AlCl_3$–NaCl–KCl molten salt containing $CrCl_2$ and/or $NiCl_2$ at 423 K. Cathodic reduction of Ni and Cr starts at potential of 0.8 and 0.15 V versus Al/Al^{3+} in the molten salt, respectively. The co-deposition of Al, Cr, and Ni occurred at potentials more negative than −0.1 V to form a mixture of intermetallic compounds of Cr_2Al, Ni_3Al, and Al_3Ni. Concentration of Cr in the deposit was enhanced to 43 at% at −0.1 V; however, concentration of Ni in the deposit was 6 at% at the same potential. The concentration of Ni further decreased with more negative potential to 1 at% at −0.4 V. The potential pulse technique enhanced the Ni concentration in the deposit to about 30 at%, due to anodic dissolution of Al content from the deposit at the higher side of potential on the potential pulse electrolysis.

Electrodeposition of Sb, Bi, Te, and their alloys in $AlCl_3$–NaCl–KCl molten salt

Hirofumi Ebe, Mikito Ueda, and Toshiaki Ohtsuka

Electrochimica Acta, 53, 100-105 (2007)

The Electrochemistry of Sb, Bi, and Te in $AlCl_3$–NaCl–KCl molten salt containing $SbCl_3$, $BiCl_3$, and/or $TeCl_4$ at 423 K was investigated by voltammetry, and electrodeposition of the three metals was performed under constant potential control in the melt. The voltammogram on a glassy carbon (GC) electrode in a melt containing 0.025 mol dm^{-3} [M] $SbCl_3$ showed a couple of redox peak corresponding to the Sb/Sb(III) redox reaction, and a stable layer of pure Sb was deposited under the constant potential control. The voltammograms in the melt containing 0.025 M $BiCl_3$ or 0.025 M $TeCl_4$ showed several redox couples. Stable deposit layers of pure Bi and Te were not obtained under the constant potential control, as the deposited layers detached from the electrode and immediately dissolved into the molten salt. Binary alloy deposition was possible in a melt containing $BiCl_3$ and $SbCl_3$, and also with $BiCl_3$ and $TeCl_4$. A stable Bi–Sb alloy deposit of metallic Sb and Bi–Sb solid solution was obtained at 0.8 and 0.9 V versus Al/Al(III) in the melt containing $BiCl_3$ and $SbCl_3$. The atomic ratio of Bi in the deposit was 37% at 0.9 V and 57% at 0.8 V. A stable Bi–Te alloy deposit was also obtained with the molten salt containing $BiCl_3$ and $TeCl_4$. The deposited Bi–Te alloy consisted of a mixture of Bi_2Te_3, BiTe, and Bi_2Te. The alloy deposit had good crystallinity and the preferential orientation was the (1 1 0) plane.

Polypyrrole Coating on Zinc for Corrosion Prevention of Zinc-coated Steels

S. Tsuchiya, M. Ueda, and T. Ohtsuka

ISIJ international, 47, 1, 151-156 (2007)

The polypyrrole (PPy) coating was prepared by constant current oxidation on zinc from aqueous solution of sodium tartrate containing sodium molybdate and pyrrole monomer to make new coating for corrosion prevention.

The coating is started with an initial formation of salt layer of zinc tartrate and/or zinc molybdate during the oxidation. Nucleation and growth of PPy takes place on the salt layer in the second stage. The PPy layer thus formed is doped by tartrate ions and/or molybdate ions, which was confirmed by depth profile measurement of glow discharge optical emission spectroscopy (GD-OES). The conductance of the coatings was as small as 1×10^{-3} S cm^{-2} for the 5 μm-thick layer probably due to the formation of the salt layer underneath the PPy layer. Corrosion test of the PPy-coated zinc electrode in 3.5 wt% NaCl solution showed that the zinc electrode was passivated and protected over 48 h by action of oxidative PPy coatingdoped by tartrate and molybdate ions.

Ellipsometry of Passive Oxide Films on Nickel in Acidic Sulfate solution

M. Iida and T, Ohtsuka,
Corrosion Science, 49, 1408-1419 (2007)

Nickel passive film has been studied in acidic sulfate solutions at pH 2.3 and 3.3 by ellipsometry. During anodic passivation followed by cathodic reduction, the roughness increases with dissolution of nickel, being indicated by gradual decrease of reflectance. However, the ellipsometric parameters, Ψ (arctan of relative amplitude ratio) and Δ (relative retardation of phase), are relatively insensitive to the roughness increase. From the change of Ψ and Δ, $\delta\Psi$ and $\delta\Delta$ during the anodic passivation and reduction, thickness of the passive oxide film was estimated with assumption of refractive index of $n_f = 2.3$ of the film. The thickness estimated is a range between 1.4 and l.7 nm in the passive potential region from 0.8 to 1.4 Vvs. RHE, having a tendency of thickening with increase of potential. Cathodic reduction at constant potential induces a change of the oxide film to an oxide film with lower refractive index of n_f=1.7, accompanied by thickening about 30% in the initial stage of reduction for 30 s. The gradual decrease of thickness takes place for the oxide with the lower refractive index in the latter stage. The potential change from the passive region to cathodic hydrogen evolution region may initially cause hydration of the passive oxide of NiO, i.e., $NiO + H_2O = Ni(OH)_2$, and during latter stage of reduction, the hydrated nickel oxide gradually dissolved.

Corrosion Products on Cut Edge Surface of Zinc-Coated Steels in Humidified Air in the Presence of NaCl Precipitate by Raman Spectroscopy

T. Ohtuska and Y. Abe

Proceeding of the Galvatech ’07, 648 (2007)

Corrosion products on zinc- and zinc alloy coated steels by atmospheric corrosion in the presence of NaCl precipitate was investigated by in-situ Raman spectroscopy. A model cut edge surface a half of which consists of the coated surface and the other consists of the bare steel was exposed to humidified air at 84 % relative humidity (RH) at 250C.

The galvanic coupling between the zinc or zinc alloy coating layer and the bare steel on which NaCl particles precipitate accelerated corrosion of zinc coating. On the zinc or zinc alloy coating at the cut edge surface, aqueous layer containing dissolved NaCl and $ZnCl_2$ initially formed. After the saturation of $ZnCl_2$, precipitate of simonkollite (zinc hydroxy-chloride) was formed. On the bare steel part at the model cut edge surface, zinc hydroxy-carbonate was formed immediately after the exposure to humidified air. The corrosion rate of the coatings under the galvanic coupling is the following order; pure Zn> Zn-12%Ni=Zn-5%Al>Zn-55%Al.

Passivation Oxide Film on Nd-Fe-B Permanent Magnets in Borate Buffer Solution by Ellipsometry

Y. Nunoko, T. Ohtsuka, and T. Sakamoto

Corrosion Science, 49, 4005-4014 (2007)

The passivation of Nd-Ge-B permanent magnet was investigated in neutral borate solution at pH 8.4. The thickness of the passive oxide film on the magnets was measured by ellipsometry and the composition was estimated by glow discharge optical emission spectroscopy (GD-OES).

The passivation of the magnets takes place in the potential region between -0.2 and 1.0 V vs. Ag/AgCl/ Sat. KCl. In the potential range, current density decays to the lower than 10^{-6} A cm^{-2} after potentiostatic oxidation for 1800 s. The passive oxide film growth is assumed to be optically simulated from a model with a homogeneous film with complex refractive index, N = 2.1-i0.086. The thickness estimated from the refractive index linearly increases with potential from 3.6 nm at -0.2 V to 7.8 nm at 1.0 V. The passive film growth follows the ionic migration model under high electric field, i.e., the Cabrera-Mott growth model. The ionic conductivity estimated from the model is about $\kappa = 1.7 \times 10^{-16}$ Ωcm^{-1}. The passive oxide film is preferentially composed of iron oxide/hydroxide. Boron and neodymium are, respectively, concentrated at the surface of the oxide film and the inner layer in the oxide film.

Characterization of rust layers exhibiting an extraordinarily high corrosion rate

T. Ohtsuka, M. Yamashita. H. Tamura, and T. Ishikawa

Symposium Report of The 160th Symposium of Corrosion and Protection,
Jpn Soc. Corros. Eng., 24-30 (2007)

The rust layer which does not have enough protection ability to corrosion of the weathering steel in atmosphere was described. The rust with low protection consists of relative large particles of iron oxy-hydroxide. The rust formed in humid atmosphere is preferentially composed of Fe_3O_4. The rust on weathering steels exposed to environment with high content of air-borne salt contains large amount of β -FeOOH.

(Japanese)

Fine Structure Rust and Effect of Alloyed Elements on Corrosion Protection of Steels

Toshiaki Ohtsuka
Feramu (Bulletin of the Iron and Steel Institute of Japan), 12, 795 (2007)

The rust layer on weathering steels works as the protection barrier against atmospheric corrosion of steels. The rust layer with high performance of corrosion protection consists of fine crystalline particles of various types FeOOH. The growth of the rust layer exposed in atmosphere takes place during the wet-dry cycles. During the wet condition, the rust of FeOOH is reduced and the substrate steel is oxidized and then during the dry condition, the reduced rust layer is reoxidized to retune to the original FeOOH rust. The growth of the rust layer is assumed to greatly depend on the reduction in the wet condition. The tendency that the rust undergoes the reduction in the wet condition will be influenced by alloyed elements such as Cu, Ni, Cr etc. and the atmospheric environment.

(Japanese)

The role of corrosion-resistant alloying elements in passivity

K. Hashimoto, K. Asami, A. Kawashima, H. Habazaki, E. Akiyama

Corros. Sci., **49**(1) 42-52 (2007).

Passivity of alloys containing corrosion-resistant elements were reviewed. Chromium and valve metals except aluminum form stable oxyhydroxide films even in aggressive hydrochloric acids. Molybdenum forms a passive MoO_2 film in the active region of stainless steels and hence decreases the active dissolution current. In the passive region of transition metals and valve metals, molybdenum is generally in the transpassive state and dissolved. However, if the outer oxyhydroxide film is stable the inner MoO_2 film is protected by the outer oxyhydroxide film and the MoO_2 film acts as the effective barrier against diffusion of matters through the film. Thus the passive current density of 30Cr–2Mo ferritic stainless steel is more than two orders of magnitude lower than that of 30Cr steel without molybdenum in 1 M HCl.

Si-C-O glass-like compound/exfoliated graphite composites for negative electrode of lithium ion battery

H. Konno, T. Morishita, C. Wan, T. Kasashima, H. Habazaki, M. Inagaki

Carbon, **45**(3) 477-483 (2007).

Two low molecular weight silicone compounds, a cyclic type having vinyl groups and a chain-type having Si–H bonds, a catalyst for curing, and a catalyst regulator were mixed. The mixture was impregnated into exfoliated graphite (EG) by sorption, and cured in air at 200 °C. By this process cross-linked silicone coatings were formed on graphite flakes. The composites of Si–C–O glass-like compounds and EG were synthesized by heat treatment of this precursor at 1000–1400 °C for 1 h in argon. The composites formed at 1000–1300 °C were amorphous by XRD and had practically the same chemical composition: Si 44–45, C 27–29, O 25–26, H < 0.5, all in mass%. The 29Si MAS-NMR spectra indicated that the compound formed at 1000 °C was mainly composed of siloxane bonds and amorphous silica, whereas in the compound formed at 1300°C, Si–C bonds and amorphous silica were predominant. The insertion/extraction characteristics of lithium ions for the electrode prepared with composite:poly(vinylidene fluoride) = 90:10 mass% were examined in 1 mol L^{-1} $LiClO_4$ solution of ethylene carbonate:diethyl carbonate = 50:50 vol%. High, 650–700 mA h g^{-1}, capacities and steady cycle performance at 50 mA g^{-1} were achieved with the composites formed at 1250–1300 °C. Capacities of the composites formed at 1200 °C and lower were initially higher but decreased with increasing number of cycles. The composites formed at 1350 °C showed good cycle performance but the capacity was about 500 mA h g^{-1} due to the formation of β-SiC. Except for the first cycle, the capacity-potential characteristics were similar to those of hard carbons and the coulomb efficiency was 95–100%. For all the composites the capacity was larger than that of graphite (372 mA h g^{-1}) in the range of 50–200 mA g^{-1}. Due to the large insertion capacity of the first cycle, the efficiency was low (60–70%) at first. By short-circuiting the working electrode to the lithium foil counter electrode for a certain period, the irreversible capacity of the first cycle was almost eliminated. It indicates that direct doping of lithium ions into composites is a promising way to increase the efficiency of the first cycle.

Synthesis and characterization of balloons and porous blocks of *β*-SiC using silicone and urethane foam

H. Konno, S. Sato, K. Kimura, H. Habazaki

J. Eur. Ceram. Soc., **27**(1) 405-412 (2007).

A process to form different shapes of *β*-SiC was developed using precursors composed of silicone compounds and urethane foam. Two types of low molecular weight silicone, a Pt catalyst for curing, and a catalyst regulator were impregnated into urethane foam chips with different porosities and bulk densities, and cured at 200 °C for 1 h in air. Formed precursors were converted into *β*-SiC by pyrolysis at 1600 °C for 1–5 h in argon. Depending on the type of urethane foam, *β*-SiC balloons and *β*-SiC blocks with high porosities and low bulk densities were obtained. In addition, fine particles of *β*-SiC smaller than 100 nm were also obtained by crushing the blocks. For a disk formed by 5 h pyrolysis at 1500 °C, N_2 gas permeability, electric conductivity, and oxidation resistance at 900 °C in air were measured. The results indicated that the disk may be used as a gas permeable heater. The process is simple, and the materials for this process are not hazardous and commercially available at low cost.

Development of anodic coatings on aluminium under sparking conditions in silicate electrolyte

F. Monfort, A. Berkani, E. Matykina, P. Skeldon, G.E. Thompson, H. Habazaki, K. Shimizu

Corros. Sci., **49**(2) 672-693 (2007).

Spark anodizing of aluminium at 5 A dm^{-2} in sodium metasilicate/potassium hydroxide electrolytes is studied, with particular emphasis on the mechanism of coating growth, using transmission electron microscopy and surface analytical techniques, with coatings typically 10 µm, or more, thick. Two-layered coatings develop by deposition of an outer layer based on amorphous silica, associated with low levels of alkali-metal species, at the coating surface and growth of an inner, mainly alumina-based, layer, with an amorphous region next to the metal/coating interface. Formation of crystalline phases in the inner layer, mainly γ-Al_2O_3, with some α-Al_2O_3 and occasional δ-Al_2O_3, is assisted by local heating, and possibly also by ionic migration processes, arising from the rapid coating growth at sites of breakdown. Due to local access of electrolyte species in channels created by breakdown events, the silicon content in the inner coating regions varies widely, ranging from negligible levels to about 10 at.%. Silica deposition at the coating surface and formation of Al_2SiO_5 and $Al_6Si_2O_{13}$ phases is promoted by increased time of anodizing and concentration of metasilicate in the electrolyte. However, at sufficiently high concentration of metasilicate and pH, when more extreme voltage fluctuations accompany breakdown, the two-layered nature of coatings is replaced by a mixture of aluminium-rich and silicon-rich regions throughout the coating thickness.

Structure of the carbon nanofilaments formed by liquid phase carbonization in porous anodic alumina template

H. Habazaki, M. Kiriu, M. Hayashi, H. Konno

Mater. Chem. Phys., **105**(2-3) 367-372 (2007).

Platelet structure carbon nanofilaments of ~30 nm in diameter have been prepared by heating a mixture of porous anodic alumina template and poly(vinyl)chloride (PVC) powders in an argon atmosphere, and the change in their structure and morphology with heat treatment temperature, ranging from 600 to 2800 ºC, has been examined using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen gas adsorption measurements. The diameter of the carbon nanofilaments formed does not change with heat treatment temperature, being in agreement with the pore diameter of the template, while their length is reduced with the temperature. The platelet-type orientation of graphene layers is evident even at 600 °C with the layer structure further developing with increasing heat treatment temperature. The carbon nanofilaments formed at lower temperatures have micropores, while those formed at higher temperatures do not have porosity. Highly graphitized carbon nanofilaments have been obtained after heat treatment at 2800 °C, with another characteristic structural feature being presence of loops at the edge of graphene layers formed at 2800 °C.

Spark Anodizing of β-Ti Alloy for Wear Resistant Coating

H. Habazaki, T. Onodera, K. Fushimi, H. Konno, K. Toyotake
Surf. Coat. Tech., 201(21), 8730-8737 (2007).

Spark anodizing of a bcc solid solution Ti–15% V–3% Al–3% Cr–3% Sn alloy has been performed in an alkaline electrolyte containing aluminate and phosphate using dc-biased ac anodizing to form a wear-resistant coating on the alloy. The coating consists mainly of Al_2TiO_5, with rutile and γ-Al_2O_3 being present as minor oxide phases. Depth profiles of the coating, examined by glow discharge optical emission spectroscopy, have revealed that aluminium species, highly enriched in the coating, distribute uniformly in the coating, while phosphorus species, incorporated from the electrolyte, are located mainly in the inner part of the coating near the coating/alloy interface. The location of the phosphorus species should be associated with the porous nature of the coating, allowing access of the electrolyte directly to the inner parts of the coating. The porosity of the coating is reduced by anodizing to high voltages. The marked improvement of the wear resistance by the coating has been demonstrated from a pin-on-disc wear test.

Formation of Porous Anodic Films on Ti-Si Alloys in Hot Phosphate-Glycerol Electrolyte

H. Habazaki, Y. Oikawa, K. Fushimi, K. Shimizu, S. Nagata, P. Skeldon, G.E. Thompson
Electrochim. Acta, **53**(4), 1775-1781 (2007).

Porous anodic films, with pore size of □10 nm, have been developed by anodizing of magnetron sputtered Ti–25 at.% Si alloy at constant formation voltages in glycerol electrolyte containing dibasic potassium phosphate at 433 K. The films, of amorphous structure, contain titanium and silicon species, as units of TiO_2 and SiO_2, throughout the film thicknesses, with negligible amounts of phosphorus species. The silicon is enriched in the film relative to the composition of the alloy, the level of enrichment suggesting that anion migration is increased in comparison with amorphous film growth at ambient temperature. In contrast to the behaviour of the alloy, essentially barrier films were formed on commercially pure titanium in the glycerol electrolyte, when a main anodic reaction was generation of oxygen, which was probably promoted by the development of anatase.

Heterogeneous Hydrogen Evolution on Corroding Fe-3 at.% Si Surface Observed by Scanning Electrochemical Microscopy

K. Fushimi, K.A. Lill, H. Habazaki

Electrochim. Acta, **52**(12), 4246-4253 (2007).

Corrosion behavior of Fe–3 at.% Si alloy in 0.01 mol dm^{-3} HCl solution was investigated by using scanning electrochemical microscopy (SECM) as well as general electrochemistry. The rate of corrosion coupled with hydrogen evolution was initially 0.44 A m^{-2} but decreased significantly with time. Localized hydrogen evolution on the specimen surface was probed by an SECM system in which a force sensor was mounted to determine the probe height from the specimen surface. SECM images revealed that hydrogen evolution took place heterogeneously on the specimen surface depending on crystallographic orientation of substrate single grains in the initial stage and then became relatively homogeneous. Finally, a heterogeneous hydrogen distribution corresponding to the appearance of localized corrosion sites was observed.

Growth of Barrier-type Anodic Titanium Oxide Incorporated with Silicon Species

M. Tauseef Tanvir, K. Fushimi, K. Shimizu, S. Nagata, P. Skeldon, G.E. Thompson, H. Habazaki
Electrochim. Acta, **52**(1), 6834-6840 (2007).

Amorphous anodic titania, stabilised by incorporation of silicon species, is shown to grow to high voltages on sputter-deposited, single-phase Ti–Si alloys during anodizing at a constant current density in ammonium pentaborate electrolyte. The films comprise two main layers, with silicon species confined to the inner layers. An amorphous-to-crystalline transition occurs at ~60V on the Ti–6 at.% Si alloy, while the transition is suppressed to voltages above 140V on alloys with 12 and 26 at.% silicon. The crystalline oxide, nucleated at a depth of □40% of the film thickness, is associated with the presence of a precursor of crystalline oxide in the pre-existing air-formed oxide. The modified structure of the air-formed oxide due to increased incorporation of silicon species suppresses the amorphous-to-crystalline transition until the onset of dielectric breakdown. The transport numbers of cations and anions during growth of the anodic oxides are independent of the concentration of silicon species in the inner layer, despite the marked change in the field strength.

A Numerical Model of Current Transients during Micro-indentation of Passive Iron Surface

K. Fushimi, T. Yamamoto, K. Azumi, M. Seo, H. Habazaki
Electrochim. Acta, **52**(24), 6901-6910 (2007).

During *in situ* micro-indentation of passive iron in pH 8.4 borate solution, a couple of anodic current peaks emerged; the first peak during loading and the second peak during unloading. The current transients, associated with rupture and repair of the passive film, were influenced by the indentation conditions. For instance, the current peak height, the current peak area and the time required for complete repassivation are strongly dependent on indentation rate. A numerical model was proposed to correlate the current transient during loading with mechanical deformation of the passive surface. The comparison between the current transient measured experimentally and that estimated from the load transient suggested that the ruptured area of passive film was about 10% of the surface area deformed by the contact with the indenter.

Fast Migration of Fluoride Ions in Growing Anodic Titanium Oxide

H. Habazaki, K. Fushimi, K. Shimizu, P. Skeldon, G.E. Thompson
Electrochem. Comm., **9**(5), 1222-1227 (2007).

The rapid inward migration of fluoride ions in growing anodic titanium oxide under a high electric field has been elucidated by anodizing a Ti–12 at% silicon alloy, where film growth proceeds at nearly 100% efficiency in selected electrolytes. Further, incorporated silicon species in the anodic film are immobile, acting as marker species. The migration rate of fluoride ions is determined precisely by three-stage anodizing, consisting of initial anodic film formation at a constant current density to 50 V in ammonium pentaborate electrolyte, subsequent incorporation of fluoride ions by reanodizing to 55 V in ammonium fluoride electrolyte and, finally, anodizing again in ammonium pentaborate electrolyte at high current efficiency. The resultant films were analyzed by glow discharge optical emission spectroscopy to reveal the depth distribution of fluoride ions and the location of the silicon marker species. The fluoride ions migrate inward at twice the rate of O^{2-} ions. Consequently, anodizing of titanium in fluoride-containing electrolytes develops a fluoride-rich layer that separates the alloy substrate from the anodic oxide, with eventual detachment of the film from the substrate.

Current Transients during Repeated Micro-indentation Test of Passive Iron Surface in pH 8.4 Borate Buffer Solution

T. Yamamoto, K. Fushimi, M. Seo, S. Tsuri, T. Adachi, H. Habazaki

Electrochem. Comm., **9**(7), 1672-1676 (2007).

Micro-indentation test was performed for passive iron surface in deaerated pH 8.4 borate solution to correlate the passive film breakdown with mechanical deformation of substrate. Loading and unloading of a conical micro-indenter to the passive surface were repeated 10 times at an identical position. Elastic–plastic deformation occurred during the first indentation, while elastic deformation is predominant during the second and following indentations. The anodic current appears at the commencement of the first loading, with the maximum current generated at the maximum load. A more obvious current peak appears when the indenter just lost the contact with the iron surface during the first unloading. The current peaks observed during the subsequent indentations decreased markedly compared with the first indentation. Thus, the passivefilm breakdown by elastic deformation of iron substrate is less significant compared with that by plastic deformation under the present conditions. There is a linear correlation between the electric charge required for repassivation of the ruptured passive film and the work for plastic deformation.

Changes in mass and stress during anodic oxidation and cathodic reduction of the Cu/Cu_2O multilayer film

M. Seo, M. Hagioi

Corros. Sci., **49** (1), 176-480 (2007)

The anodic oxidation and cathodic reduction processes of the Cu/Cu_2O multilayer film and pure Cu film in pH 8.4 borate buffer solution were analyzed by electrochemical quartz crystal microbalance (EQCM) for gravimetry and bending beam method (BBM) for stress measurement. The mass loss of the multilayer film during anodic oxidation at 0.8 V (SHE) in the passive region was less than that of the pure Cu film. The comparison between current transients and mass changes during anodic oxidation has succeeded in separating the anodic current density into two partial current densities of oxide film growth, $i_{O^{2-}}$, and of Cu^{2+} dissolution through the passive film, $i_{Cu^{2+}}$. As a result, in the case of the pure Cu film, the anodic current density was mainly due to $i_{Cu^{2+}}$, while in the case of the multilayer film, $i_{Cu^{2+}}$ was almost equal to $i_{O^{2-}}$. The compressive stress for the multilayer film was generated during anodic oxidation, while the tensile stress for the pure Cu film was generated. The mass loss of the multilayer film during cathodic reduction at a constant current density (i_c = - 20 μA cm^{-2}) was significantly less than that estimated from coulometry, suggesting that H_2O produced by cathodic reduction remained in the multilayer film. The compressive stress was generated during cathodic reduction of the multilayer film, which was ascribed to H_2O remained in the multilayer film.

Changes in surface stress of gold electrode during underpotential deposition of copper

M. Seo, M. Yamazaki

J. Solid State Electrochem., **11**(10), 1365-1373 (2007).

The changes in surface stress of the evaporated gold electrode (mainly oriented to the (111) plane) during underpotential deposition (UPD) of copper in 0.1 M sulfuric acid medium or 0.1 M perchloric acid medium with and without sulfate or chloride were measured by using a bending beam method. The surface stress maximum of gold electrode appeared during Cu-UPD. The co-adsorption of (bi)sulfate or chloride ions with copper atoms induced the compressive surface stress to promote the Cu-UPD. The factors influencing the surface stress or surface elastic strain were discussed in relation to the Cu-UPD structure.

Initial Stage of Localized Corrosion in Artificial Pits Formed with Photon Rupture on Zn -5 mass% Al Alloy Coated Steel

M. Sakairi, Y. Uchida and H. Takahasi

Corros. Sci., **49**, 2362-2370 (2007)

The photon rupture method, by which oxide film and metal are removed by focused pulsed Nd - YAG laser beam irradiation, was applied to form artificial micro pits in Zn -5 mass% Al alloy-coated steel. The zinc alloy-coated layer was removed by pulsed laser irradiation treatment for about one second in a neutral buffer solution with NaCl. The rest potential transient with the laser treatment was measured. In the early stage of the laser treatment the rest potential of zinc alloy-coated steel changed to the negative direction immediately after every irradiation of a laser pulse and then returned to the previous value. However, after the steel substrate was exposed to the solution, the rest potential moved to the positive direction immediately after every irradiation of a laser pulse and then returned to the previous value. The amplitude and duration of the potential change after the laser irradiation increased with repetition of laser irradiation, related to the pit depth and the exposed area ratio of coated layer/steel substrate. The rest potential fluctuation difference can be explained by galvanic reaction change in the artificial pit formed by laser irradiation on the Zn alloy coated.

Electrochemical Random Signal Analysis During Galvanic Corrosion of Anodized Aluminum Alloy

M. Sakairi and Y. Shimoyama

J. of Japn. Soc. for Exp. Mechanics, Special Issue, 114-119 (2007)

A new type of electrochemical random signal analysis technique was applied to galvanic corrosion of anodic oxide films formed on 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 the anodic oxide film structure on the galvanic corrosion resistance was also examined. During incubation (before localized corrosion started), both current and potential change slightly from the initial value. The incubation period of porous type anodic oxide specimens is longer than that of barrier type anodic oxide specimens. During localized corrosion, the current and potential changed with fluctuations, and the potential and the current fluctuations show good correlation. The slope of the PSD of both potential spectra of anodized specimens are about minus one (-1), after the localized corrosion has started. This technique allows observation of electrochemical impedance changes during localized corrosion.

Development of Three Electrode Type Micro-electrochemical Reactor on Anodized Aluminum with Photon Rupture and Electrochemistry

M. Sakairi, M. Yamada, T. Kikutch and H. Takahashi

Electrochim. Acta, **52**, 6268-6274 (2007)

Photon rupture with a focused single pulse of pulsed YAG-laser irradiation was used to fabricate an aluminum electrochemical micro-reactor. Porous type anodic oxide film formed on aluminum specimens was irradiated in solutions with a pulsed Nd-YAG laser beam through a convex lens to fabricate micro channels, micro-electrode, and through holes (for reference electrode, solution inlet, and outlet). During irradiation, specimens were moved by a computer controlled XYZ stage. After irradiation, the surface of the micro-channel and through hole were again treated to form anodic oxide film and the surface of the micro-electrode was treated electrochemically to provide an Au layer. The calculated volume of the micro-reactor including micro-channel and through holes is about 1.5 μl. The cyclic voltammogram of the micro-electrochemical cell was measured in $K_3Fe(CN)_6$ / $K_4Fe(CN)_6$ with both static and flowing solution at different scanning rates. The anodic and cathodic peak currents were measured and the values depended on scanning rate and ion concentration when the solution was static. With the flowing solution, limiting currents were observed and the anodic limiting current was increased with the cubic root of the solution flow rate.

Electrochemical Random Signal Analysis During Localized Corrosion of Anodized 1100 Aluminum Alloy in Chloride Environments

M. Sakairi, Y. Shimoyama and D. Nagasawa

Proc of ICEC Seoul, RNM-O-03, (2007)

A new type of electrochemical random signal (electrochemical noise) analysis technique was applied to localized corrosion of anodic oxide film formed 1100-H14 aluminum in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.01 kmol/m^3 NaCl solutions. The effect of anodic oxide film structure, porous type and barrier type, on galvanic corrosion resistance was also examined. Before localized corrosion started, incubation period for pitting corrosion, 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. While pitting corrosion, the current and potential were changed with fluctuations and the potential and the current fluctuations show a good correlation The records of the current and potential were processed by calculating the power spectrum density (PSD) by the Fast Fourier transform (FFT) method. The potential and current PSD decrease with increasing frequency, and the slopes are steeper than or equal to -1. This technique allows observation of electrochemical impedance changes during localized corrosion.

Re-passivation and initial stage of localized corrosion of metals by using photon rupture technique and electrochemistry

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

Progress in Corrosion Research, E. L. Bettini edit., Nova Sci. Publishers, Inc. NY (2007)

Study of suddenly destroyed passive oxide films and their repair is important to understand the localized corrosion of metals, especially for bio-materials. Analysis of this behavior has been carried out by monitoring potential- and current-transients after mechanical stripping of the oxide films. The mechanical film stripping methods have problems in the rate of film stripping, contamination from stripping tools, and strain or stress in the substrate.

New oxide film stripping method of a photon rupture method (focused single pulses of pulsed YAG-laser irradiation) has been developed, which resolves many of the problems caused by mechanical film stripping. The irradiation of a pulsed laser beam is able to strip oxide film at extremely high rates without contamination from the film removing tools, easily control position and size of oxide film strip. This paper will explain oxide film removal and local surface activation mechanism by the photon rupture technique, and show some experimental results of repassivation kinetics and localize corrosion of some metals.

Investigations on the local electrochemical behavior of welded stainless steels with solution flow type micro-droplet cell

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

Proc. of Eurocorr 07, No. 1130 (2007)

A new flow type of micro-droplet cell has been developed. One of the advantages of the cell is solution flows constantly so that the concentration near the working electrode will not change even in case of large current, high corrosion rate like pitting corrosion. Therefore, this new flow type of micro-droplet cell makes it possible to make accurate measurements and could be applied to investigations electrochemical behavior of base metal, heat affected zone (HAZ) and welded part.

Measurement of corrosion potentials and potentiodynamic polarization for each part of as-welded stainless steel were carried out at room temperature in 0.1 kmol/m^3 HCl. Any difference in corrosion potential was not observed between HAZ and the other parts of base metal, whereas higher current densities were observed at HAZ compared to the other parts.

Electrochemical Random Signal Analysis on Galvanic Corrosion of Anodized Aluminum Alloy in Chloride Environments

M. Sakairi and Y. Shimoyama

Proc. of Eurocorr 07, No.1131 (2007)

The new type electrochemical random signal (electrochemical noise) analysis was applied to galvanic corrosion of anodized aluminum. A porous type anodic oxide film formed 6061-T6 aluminum alloy specimens were dipped in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.3 kmol/m^3 NaCl solutions, and connected to a Pt plate to form the galvanic couple. The corrosion current and corrosion potential were measured. Before localized corrosion (pitting corrosion) started, incubation period, both current and potential slightly change as initial value with time. While pitting corrosion, the current and potential were changed with fluctuations and the potential and the current fluctuations show a good correlation. The records of current and potential were processed by calculating the power spectrum density (PSD) by the Fast Fourier transform (FFT) method. The potential and current PSD decrease with increasing frequency. The electrochemical impedance can be calculated by using the PSDs. This technique allows observation of electrochemical impedance changes during localized corrosion.

Improving of Protection of Zinc-Aluminum Alloy Coated Steels Against Corrosion by Anodizing

M. Sakairi1 and Y. Uchida

Proc. of Galvatech07, C-6-2 (2007)

Anodizing technique was applied to improve corrosion resistance of aluminum alloy coated steels. Effect of the corrosion protection by anodizing was estimated by using potentio-dynamic polarization measurements and rest-potential measurements. It is possible to form oxide film by anodizing on the coated steels, which estimated structure to be almost same as aluminum. The barrier type anodic oxide film did not affect on improving of corrosion resistance, however, the porous type anodic oxide film slightly affect on improving corrosion resistance. The pore sealing treatment, dipped in boiling distilled water, improved corrosion resistance of both type anodic oxide film formed specimens.

Nb_2O_5 Deposition on Aluminum from $NbCl_5$-used Sol and Anodizing of Nb_2O_5-coated Al

S. Koyama, T. Kikuchi, M. Sakairi, H. Takahashi, and S. Nagata

Electrochemistry, **75**, 573-575 (2007)

Formation of Nb_2O_5 films on aluminum was attempted by sol-gel coating, using $NbCl_5$ as a precursor. The structure and the dielectric properties of anodic oxide films formed on aluminum by sol-gel coating and the subsequent anodizing were examined. Anodic oxide film formed by this process was composed of an inner Al_2O_3 layer and an outer Nb_2O_5 layer. The capacitance of the anodic oxide films formed on Nb_2O_5-coated specimens was at most 34 % higher than that of anodic oxide films on aluminum without coating.

Fabrication of Three-Dimensional Platinum Microstructures with Laser Irradiation and Electrochemical Technique

T. Kikuchi, H. Takahashi, and T. Maruko

Electrochim. Acta, **52**, 2352-2358 (2007)

Three-dimensional platinum microstructures were fabricated by successive procedures: aluminum anodizing, laser irradiation, nickel / platinum electroplating, and removal of the aluminum substrate, the oxide films, and the nickel metal layer. Aluminum plates and rods were anodized in an oxalic acid solution to form porous type oxide films. The anodized specimens were immersed in a nickel electroplating solution, and then irradiated with a pulsed Nd-yttrium aluminum garnet (YAG) laser beam to remove the anodic oxide film with a three-dimensional XYZq stage. The specimens were cathodically polarized in the nickel and a platinum electroplating solution to form the metal micropattern at the laser-irradiated area. The electroplated specimens were immersed in NaOH solution to dissolve the aluminum substrate and the oxide films, and then immersed in HCl solution to dissolve the nickel deposits. A platinum grid-shaped microstructure, a microspring, and a cylindrical network microstructure with 50 – 100 μm line width were obtained successfully.

Fabrication of a three-dimensional micro-manipulator by laser irradiation and electrochemical techniques and the effect of electrolytes on its performance

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

Electrochim. Acta, **52**, 4480-4486 (2007)

Ribbon type and three-dimensional micro-actuators, consisting of three-layer structure of acrylic acid resin / Au / polypyrrole, were fabricated by aluminum anodizing, laser irradiation, and electrochemical techniques, and their performance was examined. Anodized aluminum specimens were irradiated with a pulsed Nd-YAG laser to remove anodic oxide films locally, and then an Au layer was deposited at the area where film had been removed. The subsequent electrophoretic deposition of acrylic acid resin on the Au layer, dissolution of anodic oxide film and the metal substrate, and deposition of polypyrrole on backside of Au layer by electro-polymerization enabled the fabrication of a three-layer actuator. Cyclic voltammetry of the ribbon type actuator in different electrolyte solutions showed that redox reactions of polypyrrole is accompanied with doping and dedoping of hydrated cations, and that the redox reaction strongly depends on the valency of cations in the solutions. The three-dimensional micro-actuator showed good performance as a manipulator, gripping and moving objects of several mg in solutions.

Dielectric Properties of Al-Si Composite Oxide Films Formed on Electropolished and DC-Etched Aluminum by Electrophoretic Sol-Gel Coating and Anodizing

M. Sunada, H. Takahashi, T. Kikuchi, M. Sakairi, and S. Hirai
J. Solid State Electrochem., **11**, 1375-1384 (2007)

Highly pure aluminum specimens (99.99 %) after electropolishing and DC-etching were covered with SiO_2 films by electrophoretic sol-gel coating, and were anodized in neutral boric acid / borate solutions. 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 (EIS).

It was found that electrophoretic sol-gel coating forms uniform SiO_2 films on thesurface of both electropolished and DC-etched specimens. Anodizing of specimens after electrophoretic coating lead to the formation of anodic oxide films consisting of two layres: an inner alumina layer and an outer Al-Si composite oxide layer. The anodic oxide films formed thus had slightly higher capacitances than those formed on aluminum without any coating. Higher heating temperatures after electrophoretic deposition caused the increase in capacitance of anodic oxide films more effectively. Anodizing in a boric acid solution after SiO_2 coating on DC-etched foil allowed the anode potential to reach a value higher than 1,000 V, resulting in 39% higher capacitances than those on specimens without SiO_2 film.

Microfabrication of anodic oxide film by anodizing of laser-textured aluminium

Himendra Jha, Tatsuya Kikuchi, Masatoshi Sakairi, and Hideaki Takahashi

J. Micromech. Microeng., **17,** 1949–1955 (2007)

A simple method for the fabrication of microstructures of aluminium anodic oxide film (anodic alumina) by anodizing laser-textured aluminium is demonstrated. In the process, the aluminium substrate was first textured by a low power laser beam, and then the textured aluminium was subjected for anodizing, to develop a continuous, thick porous layer on the textured surface. Microstructures with a few to several tens of micrometers depth were fabricated successfully on the anodic oxide film using various combinations of laser power density and laser scanning speed. Removing the film from the aluminium substrate enables the fabrication of various 2D and 3D microstructures from anodic alumina.

Micro-Patterning in Anodic Oxide Film on Aluminium by Laser Irradiation

Himendra Jha, Tatsuya Kikuchi, Masatoshi Sakairi, and Hideaki Takahashi

Electrochimica Acta, **52**, 4724–4733 (2007)

Microstructures such as microchannels and microchambers were fabricated on anodic oxide film of aluminium with laser direct patterning technique. The aluminium substrate covered with porous type anodic oxide film was dyed with organic dyes followed by hydro-thermal treatment. The coloured and pore sealed film shows much higher absorption then as-formed porous film, that makes possible to pattern various types of microstructures on the film by removing the upper part of the film surface by laser irradiation. Structure of the crystallized hydroxide layer on the surface of the anodic oxide film, formed during pore sealing, as well as the partial removal of anodic oxide film from the surface is described. Microstructures with depth lower than 1μm to 27μm were patterned successfully on 16 and 32μm thick anodic oxide film surfaces, using various combinations of laser power and laser scanning speed. The affect of the laser scanning speed and laser power density on the shape of the microstructures is also explained.

Laser micromachining of porous anodic alumina film

Himendra Jha, Tatsuya Kikuchi, Masatoshi Sakairi, and Hideaki Takahashi

Appl. Phys. A, **88**, 4, 617-622, (2007)

A laser direct-write process on porous anodic alumina film is carried out for the fabrication of microstructure on the film, using nanosecond, second harmonic Nd:YAG laser. Laser micromachining can be preformed in two different ways on colored and pore-sealed anodic alumina film, to generate microstructures on the film. Removal of the aluminum substrate before laser irradiation greatly improves the shape characteristics of the microstructure. The depth of microstructures can be controlled by the power and the scanning speed of the laser beam. Several structures with depths from 1 to 35μm were fabricated on anodic alumina film with good precision and reproducibility.

Area-selective Microscale Metallization on Porous Anodic Oxide Film of Aluminium

Himendra Jha, Tatsuya Kikuchi, Masatoshi Sakairi, and Hideaki Takahashi

Electrochemistry Communications, **9**, 1596–1601(2007)

A new method for micropatterning of metallic patterns on porous anodic oxide film of aluminium is described. The porous anodic oxide film was impregnated with organic dye and palladium ions before the hydrothermal pore-sealing. The surface layers formed during the pore-sealing, i.e. outer acicular hydroxide layer and a compact intermediate sub-layer trap the palladium ion underneath the layers. Exposing the palladium enriched area by the help of laser beam followed by electroless nickel deposition results the deposition of nickel on the laser-exposed part. Thickness of the deposits can be up to about 2-3μm, after about the 20 min of immersion in electroless nickel plating bath. The metallic micropatterns, formed by the method are crack free, smooth and uniform over extended length.

Oxidation behavior of Mo-Si-B in-situ composites

A. Yamauchi K. Yoshimi, Y. Murakami, K. Kurokawa and S. Hanada

Solid State Phenomena, 127, 215-220 (2007)

Isothermal oxidation behavior of Al added Mo-Si-B *in-situ* composites was investigated under Ar-20%O2 and air atmosphere over the temperature range of 1073–1673 K. The Al added Mo-Si-B composites ((Mo-8.7mol%Si-17.4mol%B) -1mol%Al) were prepared by arc-melting, and homogenized at 2073 K for 24 h in an Ar-flow atmosphere. The ternary Mo-Si-B *in-situ* composite exhibited a rapid mass loss at the initial oxidation stage and then the passive oxidation after the substrates were sealed with borosilicate glass in the temperature range of 1173–1473 K, whereas it exhibited a rapid mass gain around 1073 K. On the other hand, the Al addition significantly improved the oxidation resistance of Mo-Si-B *in-situ* composites at temperatures from 1073–1573 K. These excellent oxidation resistances are considered to be due to the rapid formation of a continuous, dense scale of Al-Si-O complex oxides.

Classification of Oxidation Behavior in Disilicides

K. Kurokawa and A. Yamauchi

Solid State Phenomena, 127, 227-232 (2007)

This study focuses on classification of structures of oxide scales formed on disilicides. The oxide scales formed on disilicides can be grouped into 3 types, (a) silica scale, (b) mixed oxide (silica + metal oxide) scale, and (c) double layered (silica/metal oxide) scale. Disilicide that forms an oxide scale of the type (a) generally show excellent oxidation resistance. As such disilicides, there are $FeSi_2$, $CoSi_2$, $MoSi_2$, WSi_2, etc. In $FeSi_2$ and $CoSi_2$, a protective silica scale must be formed due to the selective oxidation of Si, whereas in $MoSi_2$ and WSi_2 evaporation of metal oxide plays an important role for the formation of a silica scale. Oxidation of $TaSi_2$ and $NbSi_2$ belonged to the type (b), and only $CrSi_2$ the type (c).

Microstructure and Oxidation Behavior of Boron-Added WSi_2 Compact

A. Yamauchi, T. Sasaki, A. Kobayashi and K. Kurokawa

J. Japan Inst. Metals, 71, 9-15 (2007)

In order to improve the oxidation resistance of WSi_2 at 873-1573K, boron addedWSi_2 was fabricated by a spark plasma sintering method and the oxidation tests were carried out in air. The fabricated boron added WSi_2 consisted of WSi_2, Si and W_2B_5. The addition of boron into WSi_2 led to the formation of a protective borosilicate scale, resulted in improvement of the oxidation resistance. Requisite concentration of boron for the formation of a protective borosilicate scale decreased as temperature is raised. Consequently, the addition of 2 or 3 mass□ boron was the most effective for improvement of oxidation resistance of WSi_2 in the temperature range of 873-1573 K. Such effect of boron on high-temperature oxidation of WSi_2 was also discussed. (in Japanese)

Synthesis of Mo-Si-B *In-situ* Composites by Mechanical Alloying

A. Yamauchi K. Yoshimi, K. Kurokawa and S. Hanada:

J. Alloy Comp., 434-435, 420-423 (2007)

In this study, the synthesis of Mo–Si–B multi-phase alloys, so-called *in situ* composites, was attempted with the combination of mechanical alloying (MA) and spark plasma sintering (SPS) processes. MA was conducted with mixed powders of Mo, Si and B using a planetary ball mill under various milling conditions. MAed powders were characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The results obtained by XRD indicated that Mo–Si–B alloyed powders were successfully produced when elemental powders were milled at a higher milling energy. Vacuum heat treatments after the MA process promoted the formation of Mo–Si–B intermetallic phase in MAed powders. MAed powders were successfully consolidated by SPS and sound compacts of Mo_5SiB_2-based composites were synthesized.

Tie-Lined Compositions of the γ and σ Phases in a Ternary Re-Cr-Ni System at 1423 K

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

J. Japan Inst. Metals, 71, 608-614 (2007)

Compositions with tie-lines between the σ, γ, and δ phases in a ternary Re-Cr-Ni system were investigated at 1423 K by heat-treating various ternary Re-Cr-Ni alloys and a binary Re-40 at%Ni alloy in vacuum for times up to 8640 ks. The microstructures of the Re-containing alloys which had been water-quenched after various heating times were observed and their concentration profiles for Re, Cr and Ni were measured using an electron probe micro-analyzer. The Re-Cr-Ni alloys consisted of the γ phase with either the σ or δ phase. It was found that concentration profiles of the γ phase became flat after short heat treatment, but longer times of up to 8640 ks were required to achieve the same effect for the σ and δ phases.

As the Cr contents increased (i.e., Re contents decreased) in the γ phase, the solubility limits of Ni in the σ phase tie-lined with the γ phase increased from 19 at%Ni to 24 at%Ni. The δ phase tie-lined with the γ phase(11.8 at%Re, 11.5 at%Cr, and 76.7 at%Ni) has 71.1 at%Re, 3.2 at%Cr, and 25.7 at%Ni. The Ni contents in the δ phase in a binary Re-Ni system are 30 and 35 at%Ni at 1573 and 1773 K, respectively. It was concluded that compositions of the γ phase tie-lined with the σ and δ phases coincided with those in the calculated and experimentally determined phase diagrams, respectively. (in Japanese)

Phase Equilibria and Tie-Lined Compositions in a Ternary Ni-Al-Re System at 1423 K

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

J. Japan Inst. Metals, 71, 793-800 (2007)

Phase equilibria and compositions with tie-lines between the δ-Re, γ, γ ', β, Ni_2Al_3 as well as Re_2Al and $ReAl_3$ phases in a ternary Ni-Al-Re system were investigated at 1423 K by heat-treating of Ar-arc-melted Ni-Al-Re alloys in vacuum for times up to 3600 ks, followed by water-quenching and concentration measurements of Ni, Al and Re across the cross sections by using electron probe micro-analyzer (EPMA). The tie-lined compositions (at%) of each phase are summarized as follows. The δ-Re phase tie-lined with the γ phase (81.9 at%Ni, 15.9 at%Al, and 2.2 at%Re) has 18.8 at%Ni, 0.1 at%Al, and 81.1 at%Re. The δ-Re phase tie-lined with the γ ' phase (77.0 at%Ni, 21.7 at%Al, and 1.3 at%Re) has 16.2 at%Ni, 0.3 at%Al, and 83.5 at%Re. The δ-Re phase tie-lined with the β phase (50.8 at%Ni, 49.1 at%Al, and 0.1 at%Re) has 5.9 at%Ni, 1.8 at%Al, and 92.3 at%Re. The Re_2Al phase tie-lined with the β phase (45.8 at%Ni, 53.2 at%Al, and 1.0 at%Re) has 4.4 at%Ni, 33.4 at%Al, and 62.2 at%Re. The $ReAl_3$ phase tie-lined with the Ni_2Al_3 phase (39.2 at%Ni, 60.7 at%Al, and 0.1 at%Re) has 6.2 at%Ni, 75.9 at%Al, and 17.9 at%Re at 1323 K. There is no ternary intermetallic compound in the Ni-Al-Re system at 1423 K. Solubility limits of Ni and Al in the δ-Re phase in binary alloy systems are 28.0 at%Ni and (0.1□1.2)at%Al, respectively.

(in Japanese)

High Temperature Oxidation Behavior of $MoSi_2$ in Low Pressure Atmosphere

A. Ibano, K. Yoshimi1, A. Yamauchi, R. Tu, K. Maruyama, K. Kurokawa, and T. Goto

Materials Science Forum, 561-565, 427-430 (2007)

In this study, the high temperature oxidation behavior of polycrystalline $MoSi_2$ in a low-pressure atmosphere was investigated. Polycrystalline $MoSi_2$ was produced by the spark plasma sintering process. Oxidation tests were carried out at 1500°C at either 10Torr or 760Torr in an Ar-20%O_2 atmosphere. For both conditions, the weight change peaked at the initial oxidation stage, and then their weights gradually increased with increasing oxidation time. The sample weight became heavier in the ambient pressure than in the low-pressure, but the evaporation oxidation was not significant in the low-pressure condition. After the low-pressure oxidation tests, the formation of Mo_5Si_3 in the $MoSi_2$ substrate was identified. The oxidation resistance of $MoSi_2$ at 1500°C is discussed based on the obtained results.

Fundamental and Practical of High-Temperature Oxidation-1

S. Taniguchi

Bulletin of The Iron and Steel Institute of Japan, 12, 695-702 (2007)

The article aims at explaining briefly fundamental items regarding the high-temperature oxidation of metallic materials. Practical examples are chosen for deepening the understanding of the readers. This article consists of three parts; part 1 deals with fundamental issues, part 2 includes fundamental issues and oxidation of intermetallic compounds which have been receiving much attention as candidates for heat resisting materials, and part 3 explains a few phenomena encountered in the hot-rolling processes of carbon steels. Part 1 includes relationship between high-temperature structural materials and oxidation, nature and prerequisite of protective oxide scales, thermodynamic considerations, oxidation kinetics in conjunction with crystal defects of oxides and transport phenomena within them, and morphologies of scales together with internal oxidation. (in Japanese)

Material Design and Structure Control of Mo-Si Intermetallic-based Ultra High Temperature Materials

K. Yoshimi, K. Maruyama, A. Yamauchi, K. Kurokawa, N. Nomura, R. Tu, T. Goto, and S. Hanada

Journal of the JAPAN Society for Technology of Plasticity Sosei-To-Kako, 48, 887-891 (2007)

From the viewpoint of energy resource saving and reduction in CO_2 emissions, we have to attain high efficiency for energy conversion systems. However, at present this depends much on the high-temperature performance of Ni-base superalloys. Future high-temperature structural applications will require materials with increasing performances. This is the reason why various materials are candidates for replacing the current Ni-base superalloys. Mo-Si based composites are one of attractive materials for high-temperature structural applications. This review concerns about explaining the Mo-Si based composites about the relationship between material design and microstructure control for the improvement of their high-temperature strength and high-temperature oxidation resistance. (in Japanese)

X-ray Absorption Fine Structure (XAFS) Analysis of Titanium-implanted Soft Tissue

M. Uo, K. Asakura, A. Yokoyama, M. Ishikawa, K. Tamura, Y. Totsuka, T. Akasaka and F. Watari

Dental Materials Journal, 26, 268-273 (2007)

Tissues contacting Ti dental implants were subjected to X-ray absorption fine structure (XAFS) analysis to examine the chemical state of Ti transferred from the placed implant into the surrounding tissue. Nine tissues that contacted pure Ti cover screws for several months were excised in a second surgery whereby healing abutments were set. Six tissues that surrounded implants retrieved due to their failure were also excised. Ti distributions in the excised specimens were confirmed by X-ray scanning analytical microscopy (XSAM), and the specimens were subjected to fluorescence XAFS analysis to determine the chemical states of the low concentrations of Ti in the tissues surrounding Ti dental implants. Ti mostly existed in the metallic state and was considered to be debris derived from the abrasion of implant pieces during implant surgery. Oxidized forms of Ti, such as anatase and rutile, were also detected in a few specimens-and existed in either a pure state or mixed state with metallic Ti. It was concluded that the existence of Ti in the tissue did not cause implant failure. Moreover, the usefulness of XAFS for analysis of the chemical states of rarely contained elements in biological tissue was demonstrated.

The purity and thermal stability in air of metal-encapsulating carbon nanocapsules (MECNCs)

M. Uo, H. Kachi, T. Akasaka, F. Watari, Y. Sato, K. Motomiya and K. Tohji

Fullerene, Nanotubes and Carbon Nanostructures, 15, 303-309 (2007)

Rare earth elements (Y, La, Ce, Nd, Gd and Dy) encapsulated by carbon nanocapsules (CNCs) were synthesized and their purity and air oxidation stability were estimated. The purity was estimated as the rare earth carbide content. Gd- and Dy-encapsulating CNCs had higher than 30wt% and others 15 to 20wt%. Encapsulated rare earth carbide was oxidized by heating in air at 400ºC or higher. This suggested oxidation damage to the graphene capsules of CNCs.

Reaction dynamics following electron capture of chlorofluorocarbon adsorbed on water cluster: A direct density functional theory molecular dynamics study

H. Tachikawa, S. Abe

Journal of Chemical Physics, 126, 194310-194319 (2007)

The electron capture dynamics of halocarbon and its water complex have been investigated by means of the full dimensional direct density functional theory molecular dynamics method in order to shed light on the mechanism of electron capture of a halocrabon adsorbed on the ice surface. The CF_2Cl_2 moleculae and a cyclic water trimer $(H_2O)_3$ were used as halocarbon and water cluster, respectively. The dynamics calculation of CF_2Cl_2 showed that both C-Cl bonds are largely elongated after the electron capture, while one of the Cl atoms is dissociated from $CF_2Cl_2^-$ as a Cl^- ion. Almost all total available energy was transferred into the internal modes of the parent CF_2Cl radical on the product state, while the relative translational energy of Cl^- was significantly low due to the elongation of two C-Cl bonds. In the case of a halocarbon-water cluster system, the geometry optimization of neutral complex $CF_2Cl_2(H_2O)_3$ showed that one of the Cl atoms interacts with *n* orbital of water molecules of trimer and the other Cl atom existed as a dangling Cl atom. After the electron capture, only one C-Cl bond (dangling Cl atom) was rapidly elongated, whereas the other C-Cl bond is silent during the reaction. The dangling Cl atom was directly dissociated from $CF_2Cl_2^-(H_2O)_3$ as Cl^-. The fast Cl^- ion was generated from $CF_2Cl_2^-(H_2O)_3$ on he water cluster. The mechanism of the electron capture of halocarbon on water ice was discussed on the basis of the theoretical results.

The degradation of the three layered nano-carbonated hydroxyapatite/collagen/PLGA composite membrane in vitro

S.Liao, F. Watari, Y. Zhu, M. Uo, T. Akasaka, W. Wang, G. Xu, F. Cui

Dental Materials, 23, 1120–1128 (2007)

Objective. The purpose of this paperwas to investigate the in vitro biodegradation of a guided tissue regeneration composite membrane, nano-carbonated hydroxyapatite/collagen/poly(lactic-co-glycolic acid) (nCHAC/PLGA). Especially for periodontal therapy, the functional graded material (FGM) nCHAC/PLGA membrane was prepared that consisted of three layers with 8wt% nCHAC+ PLGA/4wt% nCHAC+ PLGA/PLGA, where one face of the membrane is porous, thereby allowing cell growth thereon and the opposite face of the membrane smooth, thereby inhibiting cell adhesion.

Methods. For evaluation, in vitro degradation specimens of nCHAC/PLGAwere immersed into artificial saliva solution at 37 ◦C for 1, 2, 4, 8 and 12 weeks to detect the weight loss over the period, and set pure PLGA membrane as control to compare the degraded behaviors. pH value and calcium concentration of the residual solution were measured, and morphology change was investigated by scanning electron microscopy (SEM).

Results. During the experimental period in vitro, the whole shape of the membrane could be kept for 4 weeks, after that it became powder at between 8 and 12 weeks. The results demonstrated that weight loss increased continuously with a reduction in mass of 23.1% after 4 weeks and 88% after 12 week for the nCHAC/PLGA three FGM layers composite membrane. The calcium concentration in the residual solution showed a significant increase after 4 weeks, which referred to the nano-carbonated hydroxyapatite degradation. Moreover, the pH value in the solution of the nCHAC/PLGA membrane was a little higher than that of the pure PLGA membrane, which demonstrated the possible neutralization effect from nCHAC composite for the acid outcome of PLGA in the solution. The pore structure of 8wt% nCHAC+ PLGA was enlarged on the porous surface, while the nonporous surface of pure PLGA also showed a small porous structure after increased time.

Morphological effects of variant carbonates in biomimetic hydroxyapatite

S. Liao, F. Watari, G. Xu, M. Ngiam, S. Ramakrishna and C.K. Chan

Materials Letters 61, 3624-3628, 2007

We prepared nano-carbonated hydroxyapatite (CHA) with different additions of carbonated contents at room temperature. The resulting materials were tested by X-ray diffraction (XRD), Fourier transform Infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) respectively. Results were shown that the materials were platelet-like CHA polycrystals that were similar to natural bone minerals, except for the material sample with the highest carbonated content. The presence of carbonated content in hydroxyapatite (HA) significantly decreased the crystallinity of synthesized CHA. Moreover, the morphological change of CHA was observed with the increase of carbonated content. The sequence of morphological change was from flat-like platelet, needle-arrayed platelet, particle-consisted platelet, smaller platelet, and finally spherical particle. This tendency is accordant to controllable solubility of biological HA with certain carbonated content.

Self-assembly of nano-hydroxyapatite on multi-walled,carbon nanotubes

S. Liao, G. Xu, W. Wang, F. Watari, F. Cui, S. Ramakrishna, C.K.Chan

Acta Biomaterialia 3, 669-675, 2007

Inspired by self-assembly of nano-hydroxyapatite (nHA) on collagen associated with the 67 nm periodic microstructure of collagen, we used multi-walled carbon nanotubes (MWCNTs) with approximately 40 nm bamboo periodic microstructure as a template for nHA deposition to form a nHA–MWCNT composite. The assembled apatite was analyzed by transmission electron microscopy and scanning electron microscopy. Defects that were analogous to edge dislocations along the carbon nanotubes' multi-walled surfaces were the nucleation sites for nHA after these defects had been functionalized principally into carboxylic groups. Spindle-shaped units consisting of an assembly of near parallel, fibril-like nHA polycrystals were formed and oriented at a certain angle to the long axis of the carbon nanotubes, unlike nHA–collagen in which the nHA is oriented along the longitudinal axis of the collagen molecule. One possible explanation for this difference is that there are more bonds for calcium chelation on the collagen fibril surface than on the surface of MWCNTs. Spindle-shaped units that are detached from the MWCNT template are able to maintain the ordered parallel structure of the nHA polycrystal fibril. We have thus created a self-assembled hydroxyapatite on MWCNTs.

Surface Carbonization of Titanium for Abrasion-resistant Implant Materials

Y. Zhu and F. Watari

Dental Materials Journal, 26, 245-253 (2007)

Carbide layer was formed on the surface of Ti by heating in hydrocarbon atmosphere (benzene C_6H_6) at 1000-1400°C using a high frequency induction heating method. Physical and mechanical properties of carbide-coated Ti were investigated to examine its potential as an abrasion-resistant implant material. Scanning electron microscopy (SEM) showed that the surface of Ti was covered with fine grains of 1-4 μm diameter, depending on heating conditions. In addition, carbide layer of about 1-25 μm thickness was observed on the cross-section of specimens by SEM and energy dispersive spectroscopy. Vickers hardness of surface carbide was found to be more than 2000. Further, Martens scratch test and ultrasonic scaler abrasion test showed that the indentation depth and width of carbide-coated Ti were much smaller than pure Ti, thereby confirming its high abrasion resistance. These results showed that for Ti implant materials that require high abrasion resistance, such as the abutment for dental implants, surface carbide coatings would be an effective means to improve their wear properties.

Carbon Nanotubes as Scaffolds for Cell Culture and Effect on Cellular Functions

N. Aoki, T. Akasaka, F. Watari, A. Yokoyama

Dental Materials Journal , 26, 178-185 (2007)

To investigate the dependence of biocompatibility of carbon materials on crystal structure with the aim of developing biomedical applications, single-(SW) and multi-walled (MW) carbon nanotubes (CNTs) were employed as scaffolds for cell culture and compared with graphite (GP). SaOS2 cells were used to investigate the properties and response of osteoblast-like cells. Polycarbonate membranes (PC) coated with CNTs by vacuum filtration formed a meshwork nanostructure. Cells grown on CNTs greatly extended in all directions. In terms of cell proliferation, alkaline phosphatase (ALP) activity, and protein adsorption on the substrates, CNTs showed better results than PC and GP. SW showed the best cell proliferation and total ALP. These favorable results might be attributed to the structure of CNTs and the affinity of CNTs toward proteins, thereby suggesting that CNTs could be potential scaffold materials for cell culture.

Nano-mesoscopic Structural Control in 9Cr-ODS Ferritic/martensitic Steels

S.Ukai and S. Ohtsuka

Energy Materials, 2(1), (2007)26

The development status of 9Cr–oxide dispersion strengthened (ODS) ferritic steels was reviewed, focusing on the authors' activities. This material is the most prospective cladding of the advanced high burn-up fuel elements for Japanese prototype fast breeder reactor MONJU and international Generation IV advanced fast reactors, because of their inherent radiation resistance as well as superior high temperature strength. The Y2Ti2O7 complex oxide particles in nano-scale are precipitated through the dissolution of Y2O3 by mechanical alloying processing, followed by annealing at elevated temperatures .1273 K. The formation of the unique phase, residual alphaferrite, containing nano-oxide particles, can be controlled in terms of an amount of excess oxygen and titanium. The meso-scale residual alpha–ferrite formation induces the extremely highest creep rupture strength in this class of ferritic steel tubes. The new processing for cladding manufacturing of 9Cr–ODS ferrite steels was realised by using alpha–gamma phase transformation: softening at intermediate heat treatment and equiaxed grain control at the final normalizing and tempering.

Irradiation Creep - Swelling Interaction in Modified 316 Stainless Steel up to 200 dpa

S.Ukai and S.Ohtsuka

J.Nucl. Scie. and Technol, 44(5) (2007) 743

The irradiation creep–swelling interaction parameters were precisely derived for MONJU fuel pin cladding PNC316 by irradiation tests of pressurized tubes in FFTF. It was found out that a creep–swelling coupling coefficient decreased and asymptotically approached a constant value as the swelling progresses, although it was widely believed that the irradiation creep rate could be proportional to the swelling rate. This non-proportionality in the irradiation creep–swelling interaction was investigated by means of the rate theory analyses under sequential climb-controlled glide process of dislocation due to absorption of interstitial atoms. It was clarified through a constructed robust model that the presence of a precipitate sink should upset the proportionality of the net interstitial flux into dislocations to the net vacancy flux into the voids. In addition, irradiation creep parameters derived by material irradiation was demonstrated to be applicable for reasonably predicting the irradiation creep deformation in the fuel pins.

Low Cycle Fatigue Properties of ODS Ferritic-martensitic Steels at High Temperature

S.Ukai and S.Ohtsuka

J.Nucl.Mater., 367-370 (2007) 234

Strain-controlled low cycle fatigue tests were conduced for 9Cr–ODS and 12Cr–ODS steels at 873, 923, 973 and 1023 K. The total strain ranges were controlled from 0.5% to 1.5% with strain rate of 0.1%/s. Corresponding plastic strain ranged from 0.01% to 1%. The ODS steels exhibit relatively low level of plastic strain and thus have longer fatigue life in the low total strain region compared to conventional ferritic steels such as Mod. 9Cr–1Mo steel. Neither noticeable cyclic hardening nor softening was observed in ODS steels, whilst Mod. 9Cr–1Mo steel shows an apparent cyclic softening at 873 and 923 K. This is attributable to the excellent microstructure stability due to the presence of nano-sized oxide particles dispersed in ODS steels.

Oxidation of 9Cr-Oxide Dispersion Strengthened Steel Exposed in Supercritical Water

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

J.Nucl.Mater., 371 (2007) 118

The oxidation behavior of a 9 at.% Cr oxide dispersion strengthened (ODS) ferritic/martensitic (F/M) steel exposed to supercritical water at different application temperatures was examined. For comparison, two non-ODS F/M steels HCM12A (12 at.% Cr) and NF616 (9 at.% Cr) were also examined. The oxidized samples were characterized using gravimetry, scanning electron microscopy/energy dispersive X-ray spectroscopy, X-ray diffraction, electron back-scatter diffraction and transmission electron microscopy/selected area diffraction. A lower weight gain was consistently observed in 9Cr ODS steel at 500 _C and 600 _C. During exposure, the formation of an internal oxidation layer in the 9Cr ODS steel played a key role in establishing the oxidation behavior. In the 600 _C exposure, grain boundary diffusion of cations may no longer proceed dominantly as it did in the 500 _C exposure. Volume diffusion was likely accelerated and the bulk grains became a more important path for element migration, and the benefit from a small quantity of yttrium (0.28 wt%) in the steel became limited. However, because of the fine grain size of the 9Cr ODS steel, Cr quickly segregated to the ferritic grain boundary region in the internal oxidation layer and especially to the internal oxidation layer/base steel interface, resulting in the formation of Cr-enriched spinel ribbons and a Cr-enriched continuous spinel layer. The microstructure that developed slows down the further diffusion of both cations and anions at 600 C.

Time Dependence of Corrosion in Steels for Use in Lead-alloy Cooled Reactors

M.Machut, K.Sridharan, N.Li, S.Ukai and T.Allen

J.Nucl.Mater, 371 (2007) 134

Stability of the protective oxide layer is critical for the long-term performance of cladding and structural components in lead-alloy cooled nuclear systems. Measurements have shown that removal of the outer magnetite layer is a significant effect at higher temperatures in flowing lead–bismuth. Developing a predictive capability for oxide thickness and materialremoval is therefore needed. A model for the corrosion of steels in liquid lead-alloys has been employed to assist in materialsdevelopment for application in the Generation IV Lead-cooled Fast Reactor (LFR). Data from corrosion tests ofsteels in Los Alamos National Laboratory’s DELTA Loop is used to benchmark the model and to obtain predictionsof long-term material’s corrosion performance. The model is based on modifications of Wagner’s diffusion based oxidation theory and Tedmon’s equation for high-temperature oxidation with scale removal. Theoretically and experimentallyobtained values for parabolic oxide growth rate, mass transfer corrosion rate, and long-term material thinning rates arepresented and compared to the literature.

Properties of Friction Welding between ODS and PNC-FMS

T.Uwaba, S.Ukai, T.Nakai, M.Fujiwara

J.Nucl.Mater., 367-370 (2007) 1213

Friction welding of oxide-dispersion-strengthened-steel (ODS) and ferritic–martensitic 11Cr–0.5Mo–2W, V, Nb steel (PNC-FMS) was examined to investigate the feasibility of the welding of this alloy combination. Forge pressure was varied in the welding test to investigate the effect on the soundness of the weld joint. Post-weld heat treatment was necessary for the weld joint because of quench hardening in the heat-affected zone in the as-welded condition. The welds were crosssectioned and examined to determine their metallurgical structure, hardness and tensile strength. Since the heat treatment produced a softened zone near the weld interface, the furnace-cooling rate was investigated to determine the rate at which the softening did not occur. The weld joints were cold-rolled and the soundness of the weld interface was determined by tensile testing the cold-rolled weld joints.

Nano-mesoscopic structural control of 9Cr ODS martensitic steelfor improving creep strength

S. Ohtsuka, S.Ukai, M. Fujiwara, H. Sakasegawa, T. Kaito and T. Narita

J.Nucl.Mater., 367-370 (2007) 160

This paper describes the effect on creep strength and microstructure of 9Cr-oxide dispersion strengthened martensitic steel (9Cr-ODS steel) produced by differences in titanium concentration and consolidation temperature. The increase of titanium concentration to 0.30–0.35 wt% was shown to provide considerable improvement of creep strength accompanied by the increase of residual-a ferrite. The elevation of hot-extrusion temperature degraded the creep strength, however, it appeared to increase the volume fraction of residual-a ferrite. The creep deformation process of 9Cr-ODS steel was discussed to explain these results based on microstructure observations.

Investigation of Y_2O_3 Distribution in Welding Joints of Thin Claddings from Dispersion-hardened Steel

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Atomic Energy, 102(6) (2007) 430

The results of investigations of the yttrium oxide distribution in the weld joints of dispersion-hardened steel cladding, manufactured by the powder metallurgy method, are presented. It is shown that when using the methods of fusing welding of thin-walled fuel-element cladding, the content and uniformity of the yttrium oxide distribution in the metal of a seam changes as compared with the cladding metal. The concentration and uniformity of the yttrium oxide distribution in the section of a weld joint obtained by pulsed laser welding is higher than that obtained with argon-arc welding.

Microstructural Development of a Heavily Neutron-irradiated ODS Ferritic Steel (MA957) at Elevated Temperature

S.Yamashita, N.Akasaka, S.Ukai, and S.Ohnuki

J.Nucl.Mater., 367-370 (2007) 202

Microstructural observation was performed on a neutron-irradiated oxide dispersion strengthened (ODS) ferritic steel with emphasis on oxide behavior, including phase stability under irradiation at elevated temperature (973 K). Transmission electron microscopy observation of the Y–Ti complex oxide particles showed they were fine (40 nm) whereas the Ti-oxide particles were relatively coarse (300 nm). Dispersion parameters of oxide particles, such as mean size and number density, changed due to irradiation. This implies recoil resolution of the oxide particles. When irradiated at 973 K, some Y–Ti complex oxides survived and interacted with the dislocation structures, which delayed the dislocation recovery and stabilized the elongated grain structure. It is considered that oxide particles could be effective pinning points of dislocations in motion under irradiation to a dose of 100 dpa.

Creep Constitutive Equation of Dual Phase 9Cr ODS Steel

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J.Nucl.Mater., 373(1-3) (2007) 82

9Cr-ODS (oxide dispersion strengthened) steels developed by JAEA (Japan Atomic Energy Agency) have superior creep properties compared with conventional heat resistant steels. The ODS steels can enormously contribute to practical applications of fast breeder reactors and more attractive fusion reactors. Key issues are developments of material processing procedures for mass production and creep life prediction methods in present R&D. In this study, formulation of creep constitutive equation was performed against the backdrop. The 9Cr-ODS steel displaying an excellent creep property is a dual phase steel. The ODS steel is strengthened by the d ferrite which has a finer dispersion of oxide particles and shows a higher hardness than the a0 martensite. The d ferrite functions as a reinforcement in the dual phase 9Cr-ODS steel. Its creep behavior is very unique and cannot be interpreted by conventional theories of heat resistant steels. Alternative qualitative model of creep mechanism was formulated at the start of this study using the results of microstructural observations. Based on the alternative creep mechanism model, a novel creep constitutive equation was formulated using the exponential type creep equation extended by a law of mixture.

High Burnup Fuel Cladding Materials R&D for Advanced Nuclear Systems

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J.Nucl.Scie. and Technol., 44(3) (2007) 323

Cladding materials development is crucial to realize highly efficient and high-burnup operation over 100GWd/t of so called Generation IV nuclear energy systems, such as supercritical-water-cooled reactor (SCWR) and lead-cooled fast reactor (LFR). Oxide dispersion strengthening (ODS) ferritic/martensitic steels, which contain 9–12%Cr, show rather high resistance to neutron irradiation embrittlement and high strength at elevated temperatures. However, their corrosion resistance is not good enough in SCW and in lead at high temperatures. In order to improve corrosion resistance of the ODS steels in such environment, high-Cr ODS steels have been developed at Kyoto University. An increase in Cr content resulted in a drastic improvement of corrosion resistance in SCW and in lead, while it was expected to cause an enhancement of aging embrittlement as well as irradiation embrittlement. Anisotropy in tensile properties is another issue. In order to overwhelm these issues, surveillance tests of the material performance have been performed for high Cr-ODS steels produced by new processing technologies. It is demonstrated that high- Cr ODS steels have a high potential as fuel cladding materials for SCWR and LFR with high efficiency and high burnup

Recent Progress in US-Japan Collaborative Reseach on Ferritic Steels R&D

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J.Nucl.Mater., 367-370 (2007) 60

The mechanisms of irradiation embrittlement of two Japanese RAFSs were different from each other. The larger DBTT shift observed in F82H is interpreted by means of both hardening effects and a reduction of cleavage fracture stress by M23C6 carbides precipitation along lath block and packet boundaries, while that of JLF-1 is due to only the hardening effect. Dimensional change measurement during in-pile creep tests revealed the creep strain of F82H was limited at 300 _C. Performance of the weld bond under neutron irradiation will be critical to determine the life time of blanket structural components. Application of the ODS steels, which are resistant to corrosion in supercritical pressurized water, to the water-cooled blanket is essential to increase thermal efficiency of the blanket systems beyond DEMO. The coupling of RAFS and ODS steel could be effective to realize a highly efficient fusion blanket.

Particle size effects in mechanically alloyed 9Cr ODS steel powder

H. Sakasegawa, S. Ohtsuka, S. Ukai, H. Tanigawa, M. Fujiwara, H. Ogiwara, and A.Kohayama

J.Nucl.Mater, 367-370 (2007) 185

The superior creep properties of 9Cr ODS (Oxide Dispersion Strengthened) steels result from small oxide particles dispersed in the matrix. Thus many investigations have studied the creep properties by focusing on the oxide particle distribution, but these results are not sufficient to clarify the creep mechanism and to develop material processing procedures for mass production. Potential microstructural features affecting the creep properties should be studied. The 9Cr ODS steel has many potential microstructural features, for example, PPB (Prior Particle Boundary) pores, precipitates, and two matrix phases. In particular, PPB pores link up and develop into large creep cavities. Therefore, particle size classification of mechanically alloying (MA) produced powders was performed to control PPB. Contrary to our expectations, the particle size classification did not only affect PPB creep cavities, but also other microstructural features. MA powder particle size effects on microstructural features and the creep properties were studied.

Formation of Ni Aluminide Surface Layer Containing Zr by Molten-Salt Electrodeposition and Cyclic-Oxidation Resistance

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J.Japan Inst. Metals, **71**, 357-361 (2007)

The formation of a Ni aluminide coating layer containing Zr on a Ni substrate was attempted by the electrodeposition of Zr and Al. The cyclic oxidation resistance of the Ni covered with the coating was then evaluated. Zr and Al were deposited by molten salt electrolysis. For the sample treated with the Al deposition a layer consisting of Ni_2Al_3 was uniformly formed. On the other hand for the sample treated with the Zr deposition, followed by the Al deposition, a layer consisting of Ni_2Al_3 and a Ni aliminide layer containing of Zr in the Ni_2Al_3 layer were formed. Furthermore, when the Zr electrodeposition conditions were changed, the concentration of Zr in the Ni aluminide layer containing Zr, formed on the surface, changed. The cyclic oxidation test showed that for the sample with the Al deposition, the mass reduction due to scale exfoliation took place, whereas for the sample treated with a small deposit of Zr, followed by Al deposition , no mass reduction was observed. For this sample, after cyclic oxidation test, a scale consisting of α-Al_2O_3 adhering to the substrate was formed. Consequently, it was found that the cyclic oxidation resistance of the Ni was improved by a small of Zr, followed by Al deposition.

Deformation Behavior of ReCr sigma Phase Diffusion Barrier on Ni-Based Superalloy

S. Miura, K. Ohkubo, T. Mohri, T. Yoshioka and T. Narita

J. Mater. Res. Soc. Symp. Proc., 980 (2007)

In order to attain a better oxidation resistance of Ni-based superalloy s s for high performance engines, a ReCr-based σ-phase diffusion barrier coation between the MCrAlY bond coat (Al reservoir) layer and a Ni-based superalloy substrate has been proposed to suppress the diffusion of Al and other elements. The deformation behavior of TMS-82+ superalloy specimen with coating layers composed of an Al-rich surface layer (corresponding to a bond coat) and a ReCr σ-phase inner layer is investigated. In- situ observation of the bending tests using a laser scanning confocal microscopy revealed that the crack formation in the Al-rich surface layer(s) on the tension side of the bend specimen occurs at an early stage of bending. On the other hand, small cracks in the σ-phase layer under the Al-rich surface layer(s) are formed at the slip traces in the Ni-based superalloy single crystal substrate. This sugegests a good adheasion between the σ-phase and the Ni-based superalloy. At the compression side, in both the Al-rich surface layer(s) and the σ-phase layer no cracking was observed until the Al-rich surface layer(s) shows buckling.

Effect of Oxidation Resistant Coating on the Deformation Behavior of TiAl Alloys at 1173 K in Air

T. Nishimoto, S. Hayashi and T. Narita

J.Japan Inst. Metals, **71**, 25-33 (2007)

The effects of coating on the deformation and oxidation behavior of Ti-50Al alloy were investigated at 1173 K in air at a constant loading of 30 MPa. The coating was formed by a two-step Cr/Al diffusion treatment and consisted of an outermost TiAl2 layer, an outer Al-rich γ layer, an intermediate γ, Laves and β mixture layer, and a Cr diffusion zone. Tensile tests were also carried out with sole Cr or Al coated TiAl and uncoated TiAl at 1173 K for comparison purposes. 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 extensive exfoliation. 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 the γ, β, and Laves phase mixture

The Effect of an Applied External Tensile Stress on the Oxidation Behavior of a Nickel-Base Alloy with a Re-base Diffusion-barrier-coating

M. Sakata, S. Hayashi, T. Nishimoto, T. Yoshioka and T. Narita

Oxid Met, **68**, 295-311, (2007)

A diffusion-barrier-coating system with a duplex layer structure comprised of an inner Re-base alloy layer and an outer β-NiAl layer was formed on the Ni-Mo alloy, Hastelloy-X. Alloy specimens with and without the coating were oxidized at 970˚C in air for up to 200 h with an imposed tensile stress of 22.5 MPa. The oxidation behavior under the stress-free condition was also investigated for comparison purposes. Strain rates of the specimens with a diffusion-barrier-coating system decreased rapidly for about 5 h, followed by a slow creep-deformation with a strain of 3.5% and strain rates of (0.7-0.2)×10-7/s for 200 h. There was little change in both the coating structure and the composition (at%) of the inner Re-base alloy layer. Considering the creep behavior of the uncoated alloy, as well as the fact that there were few cracks and flaws in the Re-base alloy layer, it was concluded that this inner layer was subject to creep-deformation along with the alloy substrate. The external scale on the coated alloy consisted mainly of θ-Al_2O_3 at the early stage of the oxidation/deformation, and with further oxidation the surface scale formed a duplex layer structure consisting of outer plate-like θ-Al_2O_3 and inner equi-axed Al_2O_3. There was exfoliation of the outer θ-Al_2O_3 scale during the creep deformation. After the 200 h oxidation the outer β-NiAl contained (40-50)% Al, while the alloy substrate near the inner layer had less than 1 at% Al. It was found that the Re-base alloy layer acted an effective barrier against inward Al diffusion and outer diffusion of allying elements.

Formation of a Rhenium-base Diffusion-barrier-coating System on Ni-base Single Crystal Superalloy and its Stability at 1,423 K

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Oxid Met, **68**, 313-329, (2007)

A diffusion-barrier-coating system having a duplex structure comprised of an inner Re(W)-Cr-Ni layer and an outer Ni-aluminide layer was formed on a forth generation, single-crystal Ni-base superalloy by using electroplating of Re(Ni) and Ni(W) films, Al- and Cr- (high-Cr and low-Cr) pack cementations, and a combination of the two treatments. With the ReW-high-Cr coating, fine needle- or plate-like precipitates formed in the alloy substrate below the inner Re(W, Cr, Ni) layer, while there was little of this precipitate with the ReW-low-Cr pack-cementation coating. The inner, Re-base alloy layer in the ReW-high-Cr coating was identified to be a σ-(Re, Cr, W, Ni) phase, while the inner layer of the ReW-low-Cr was a mixture of σ-(Re, Cr, W, Ni) and δ-Re(Cr, W, Ni) phases. After heating the coated alloys at 1,150˚C for 100 h in air, the outer Al reservoir layer became β-NiAl containing (31-33) Al with α-Cr particles and fine precipitates of γ'-Ni_3Al with both the ReW-high-Cr and ReW-low-Cr treatments. In the case of the ReW-high-Cr coating there were numerous light-colored, needle-like precipitates formed deep in the alloy substrate under the inner layer, while in the case of the ReW-low-Cr coating γ' appeared near the inner layer. It was found that the inner, Re-base alloy layer acted as a diffusion barrier, and that its structure was maintained with little change in composition after 100 h of oxidation at 1,150˚C.

Formation and Oxidation Behavior of a Diffusion-Barrier-Coating System on a Ni-Mo base Alloy at 1,373 K in Air

Y. Katsumata, T. Yoshioka, Kemas Zaini Thosin, T. Nishimoto, T. Izumi, S. Hayashi and T. Narita

Oxid Met, **68**, 331-342 (2007)

A Ni-aluminide / Re-base diffusion-barrier-coating system and, for comparison, a sole Ni-aluminide coating were formed on the Ni-Mo based alloy Hastelloy-X, and the oxidation behavior of the coated alloys was investigated in air at 1,100˚C for up to 400 h. After 100 h of oxidation the diffusion-barrier-coating system consisted of a duplex structure comprised of an inner σ-(Re, Mo, Cr, Ni) and an outer β-NiAl layers and covered by a protective Al_2O_3 scale. By contrast, the Ni-aluminide coating had degraded, forming a reaction diffusion zone, γ-Ni(Cr, Mo, Fe, Al), with voids, and the external scale exfoliated extensively. After 400 h of oxidation of the diffusion-barrier-coating system, an intermediate reaction-diffusion zone was present. The Mo of the alloy substrate was enriched in the inner σ-layer, changing it from Re-base alloy to a Mo-base alloy. The Mo-base alloy appeared to enhance both inward-Al diffusion and outward diffusion of alloying elements such as Mo, Fe, and Cr to form the intermediate reaction-diffusion zone. The outer layer consisted mainly of β-NiAl with channels of γ-Ni(Cr, Mo, Fe, Al). It was concluded that the Re-base alloy such as a σ-phase in the Ni-Cr-Re system acts as an effective diffusion-barrier layer, but that is not the case for the Mo-base alloy layer.

Oxidation Behavior of Nickel-Base Single-Crystal Superalloy with Rhenium-Base Diffusion Barrier Coating System at 1,423 K in Air

T. Narita, F. Lang, Kemas Zaini Thosin, T. Yoshioka, T. Izumi, H. Yakuwa and S. Hayashi

Oxid Met, **68**, 343-363 (2007)

The oxidation behavior of the nickel-base single-crystal superalloy TMS-82+ coated with a duplex Re(W)-Cr-Ni / Ni(Cr)-Al layer was investigated in air at 1,150˚C for up to 100 h. The coating layer was formed by electroplating Re(Ni) and Ni(W) films on the alloy, followed by Cr-pack cementation at 1,300˚C, and as a result, forming a continuous Re(W)-Cr-Ni diffusion-barrier layer. A Ni film containing fine Zr particles was then electroplated on the duplex layer, followed by Al pack cementation at 1,000˚C for 1 and 5 h to form an Al reservoir layer with a duplex Ni_2Al_3/γ-Ni layer, which changed quickly to γ-Ni phase containing (10～13)at.% Al for the 1 h Al-pack coat and a mixture of γ'-Ni_3Al and β-NiAl phases for the 5 h Al-pack coat during high-temperature oxidation. A protective α-Al2O3 scale formed during oxidation at 1,150˚C in air, and parabolic rate constants of 7.4 × 10-11 and 6.6 × 10-10 $kg^2m^{-4}s^{-1}$ were obtained for the 1 h- and 5 h- Al pack-coatings, respectively. There was little change in the structures of the superalloy substrate after oxidation at 1,150˚C in air for up to 100 h. It was found that the Re(W)-Cr-Ni layer remained stable, acting as a diffusion barrier between the alloy substrate and Al reservoir layers.

Thermal Stability of a Rhenium-Based Diffusion Barrier Coating Layer on a Ni-Based Superalloy

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Materials Transactions, **48**, 127-132 (2007)

The thermal stability of coatings containing a Re-based diffusion barrier layer was investigated by surface and cross-sectional analysis methods. A Re-based barrier layer accompanied by an outer Ni-Cr-Al layer was prepared by electrolytic plating onto a Ni-based superalloy, followed by Cr-pack cementation in vacuum at 1523 K. Vacuum annealing was carried out at 1423 K for 25 h. Another type of coating specimen, with an additional Al reservoir layer on the Re-based barrier layer, was oxidized in air for 25 one-hour cycles at 1423 K. EDXRF, XRD, SEM, EDS and EPMA were used for analysis to evaluate the effects of the heat treatments. It was found that the barrier layer decomposed at high temperature when it was coated with a low-Al Ni-Cr-Al phase, but had good stability when it was adjacent to a high-Al Ni-Cr-Al phase.

Effect of synthesis routes on the performance of hydrated Mn(IV) oxide-exfoliated graphite composites for electrochemical capacitors

Chuanyun Wan, Kazuhisa Azumi, Hidetaka Konno

J. Applied Electrochemistry, **37** (2007) 1055–1061

MnO_2•nH_2O-EG composites for electro- chemical capacitors were prepared using commercially available low cost exfoliated graphite (EG) as a conductive substrate, and (a) potassium permanganate and (b) manganese(II) acetate solutions by two different routes. Method (1) was addition of EG to (a), followed by 1 h stirring and then slow addition of (b), and in Method (2) the solutions (a) and (b) were swapped. Using Method (1) submicron or smaller sized MnO_2•nH_2O particles having mesopores were formed, whereas Method (2) produced lumps of aggregated particles of several tens microns without mesopores, though specific surface areas were not very different and both were similar by XRD. Although EG alone showed only about 2 F g^{-1}, the capacitance per net amount of MnO_2 in 1 mol L^{-1} Na_2SO_4 solution increased proportionally with EG content and was always larger by Method (1) than Method (2), that is, the utilization ratio of MnO_2 increased with EG content and the effect was more prominent in the case of Method (1). The results indicated that EG is a good conductive material for MnO_2•nH_2O electrochemical capacitors if appropriate synthesis processes are used. The performance of the composites strongly depends on synthesis method, even using the same raw materials. It was suggested that the morphology of the products was a primary factor leading to different performance rather than composition.

Hydrated Mn(IV) oxide-exfoliated graphite composites for electrochemical capacitor

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Electrochimica Acta, **52** (9) (2007) pp.3061-3066.

Commercially available low cost exfoliated graphite (EG, nominal diameter130 μm) was used as a conductive substrate for electrochemical capacitor of hydrated Mn(IV) oxide, MnO_2•*n*H_2O. The MnO_2•*n*H_2O–EG composites were prepared by addition of EG to potassium permanganate solution, followed by 1h stirring and then slow addition of manganese(II) acetate solution. By this procedure submicro meter or smaller sized MnO_2•*n*H_2O particles having mesopores of 6–12 nm in diameter were formed on the graphite sheets of EG. Although EG alone showed only about 2Fg^{-1}, the composites showed good rectangular cyclic voltammograms at 2–20 mV s^{-1} in 1mol L^{-1} Na_2SO_4. The capacitance pernet amount of MnO_2 increased proportionally with EG content, that is, utilization ratio of MnO_2 increased with EG content. The composites of MnO_2•*n*H_2O and smaller diameter of EG (nominal diameter 45 μm) or artificial graphite powder (average diameter 3.7 μm) showed fairly good performance at 2 mVs^{-1}, but with increasing potential scan rate the rectangular shape was distorted and capacitance decreased drastically. The results implies that sheet-like structure is more effective than small particles as conductive materials, when the formation procedure of composite is the same. Large sized EG may be a promising conductive material for electrochemical capacitors.

Improvement in stannate chemical conversion coatings on AZ91 D magnesium alloy using the potentiostatic technique

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Electrochimica Acta, **53**(2) (2007) 1006-1012.

The deposition of stannate chemical conversion coatings on AZ91 D magnesium alloy by using the potentiostatic technique was investigated to improve uniformity and corrosion protection performance of the coating film. It was found that anodic polarization during the stannate conversion process accelerated dissolution of magnesium ions and promoted deposition of the coating film. Optimal polarization potential was explored as a function of corrosion protection performance evaluated by potentiodynamic polarization curves in borate buffer solution. Scanning electron microscope observation and electrochemical corrosion tests of the stannate-coated samples confirmed significant improvement in uniformity and corrosion resistance of coatings deposited by the potentiostatic technique compared to those of coatings deposited by the simple immersion method.

The Structures and Electronic States of Zinc-Water Clusters $Zn_n(H_2O)_m$ (n=1-32 and m=1-3)

H. Tachikawa, K. Iokibe, K. Azumi, and H. Kawabata
Phys. Chem. Chem, Phys., **9** (2007) 3978-3984.

Ab initio and Density Functional Theory (DFT) calculations have been carried out for zinc–water clusters Zn_n–$(H^2O)_m$ (n = 1–32 and m = 1–3, where n and m are the numbers of zinc atoms and water molecules, respectively) to elucidate the structure and electronic states of the clusters and the interaction of zinc cluster with water molecules. The binding energies of H_2O to zinc clusters were small at n = 2–3 (2.3–4.2 kcal mol^{-1}), whereas the energy increased significantly in n = 4 (9.0 kcal mol^{-1}). Also, the binding nature of H_2O was changed at n = 4. The cluster size dependency of the binding energy of H_2O accorded well with that of the natural population of electrons in the 4p orbital of the zinc atom. In the larger clusters ($n >$ 20), it was found that the zinc atoms in surface regions of the zinc cluster have a positive charge, whereas those in the interior region have a negative charge with the large electron population in the 4p orbital. The interaction of H_2O with the zinc clusters were discussed on the basis of the theoretical results.

Surface diffusion of Zn adatom on Zn(001) surface: A DFT study

K. Iokibe, K. Azumi and H. Tachikawa
J. Phys. Chem. C, 111 (2007) 13510-13516.

The adsorption and diffusion of a Zn atom on a Zn(001) surface has been investigated theoretically by using first-principles periodic boundary condition calculations to elucidate the mechanism of crystal growth of zinc in a Zn surface. Three surface models, terrace, step, and kink, of the Zn(001) surface were considered as adsorption sites in the present study. The most stable site in the terrace model was the on-top site, where the zinc adatom is bound to only one zinc atom of the surface. The activation barrier between the on-top site and the next on-top site was negligibly low (the activation energy is 44 meV at the PW91/LANL2DZ level), suggesting that the Zn adatom diffuses easily on the Zn(001) surface. The Zn adatom was more stabilized at the step site (752 meV) and kink site (935 meV) with respect to the on-top site. It was found that the magnitude of 4s-4p orbital mixing of the Zn adatom (hybridization) is strongly related to the binding energy. The mechanism of the adsorption of Zn on Zn(001) surfaces was discussed on the basis of theoretical results.

Effect of Surface Pretreatment by Acid Pickling on the Density of Stannate Conversion Coatings Formed on AZ91 D Magnesium Alloy

Hassan H. Elsentriecy, K. Azumi and H. Konno

Surface Coating and Technology, **202**[3] (2007) 532-537

Hydrofluoric and hydrochloric acid solutions and a mixture of them were tested as pickling solutions for AZ91 D Mg alloy before application of stannate coatings. Optical microscopy and energy dispersive X-ray spectroscopy (EDX) of the alloy surface after the pickling process showed that the Mg-rich α phase dissolved preferentially rather than the Al-rich β phase in hydrochloric acid solution. On the other hand, in hydrofluoric acid solution, Mg dissolved in a form of pitting corrosion. Pickling pretreatment with a mixture of these acids at an optimal concentration and an optimal pickling time resulted in relatively uniform dissolution of the alloy surface. The potentiodynamic polarization technique was used to investigate the anodic behavior of the uncoated and coated magnesium alloy in borate buffer solution. The morphology of the coatings was observed using a scanning electron microscope (SEM) before and after corrosion tests. The experimental results showed that coating film density and corrosion resistance of stannate-coated samples prepared with pickling pretreatment were improved compared with those of the coated sample without pickling pretreatment.

Effect of Copper Pretreatment on the Double Zincate Process of Aluminum Alloy Films

K. Azumi, S. Egoshi, S. Kawashima, and Y. Koyama

J. Electrochemical Society, **154** (2007) D220-D226.

Etching pretreatment in H_2SO_4 + $CuSO_4$ solution was applied to magnetron sputter-deposited Al–Si alloy films formed on a glass plate to improve uniformity of Zn deposition in the double zincate process. In the etching process, a small amount of Cu was deposited on the alloy surface at a very high density to accompanying Al dissolution. These deposits acted as nucleation seeds for Zn deposition, resulting in uniform, fine and thin Zn layers on Al alloys in a zincate process. This effect was more prominent on Al alloys containing 2.0 or 2.6 atom % of Si than on those containing 0 or 1.0 atom % of Si. Such a discrepancy was caused by increased Cu deposition on Al–Si alloys with relatively high Si concentration.

Removal of oxide layer on SUS304 using high-voltage discharging polarization

K. Azumi, A. Kanada, M. Seo, T. Mizuno

Electrochimica Acta, **52** (2007) 4463-4470.

SUS304 stainless steel rods were oxidized at 1073 K in air to form oxide film and then immersed in NaOH solution to be polarized cathodically at a cell voltage of 125 V. The electrode emitted light due to the formation of a plasma state at the interface between the electrode surface and the solution caused by the strong electric field applied to the interface. Atomic emission lines of Fe, Cr and Ni were found in the light spectra. The intensity of light was stronger on the oxide layer than on the metal surface. From the time transient of intensities of light, the oxide layer was found to be almost removed from the surface after high-voltage polarization within 10 s. From comparison of experimental results with a model calculation assuming the sputtering of oxide film with bombardment by charged particles in the plasma phase, it was estimated that the removal of surface oxide layer was done by micro-arc discharge mechanism rather than continuous sputtering. Because the formation of micro-arc preferentially occurred on the oxide layer rather than on metal surface, the removal of oxide layer from the surface was considerably rapid. On the other hand, at the point where micro-arc discharge occurred, melting of metal surface was found.

A DFT study on the structures and electronic states of zinc cluster Znn (n = 2–32)

K. Iokibe, H. Tachikawa and K. Azumi
J. Phys. B: At. Mol.Opt.Phys., **40** (2007) 427-436.

Ab-initio and density functional theory (DFT) calculations have been carried out for zinc clusters Zn_n (n = 2–32, n is the number of atoms to form a cluster) to elucidate the structure and electronic charge states of the clusters and the mechanism of clustering. The binding energies of Zn atoms were negligibly small at n = 2–3, whereas the energy increased significantly at n = 4 (the first transition). The second transition occurred at n = 8–16. In the larger clusters (n = 16–32), the binding energy increased slightly with increasing cluster size (n). The cluster size dependence of the binding energy and bond length between zinc atoms agreed well with that of the natural population of electrons in the 4p orbital of the zinc atom. In the larger clusters ($n > 20$), it was found that the zinc atoms in the surface region of the cluster have a positive charge, whereas those in the interior region have a negative charge with a large population in the 4p orbital. The formation mechanism of zinc clusters was discussed on the basis of the theoretical results.

Dissolution of Ti Wires in Sulphuric Acid and Hydrochloric Acid Solutions

K. Azumi, M. Nakajima, K. Okamoto and M. Seo
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Ti wire electrodes were immersed in acidic solutions containing H2SO4 and HCl of various concentrations at 353 K to evaluate corrosion rate by measurement of electric resistance change (resistometry). Addition of hydrochloric acid to sulphuric acid solution promoted depassivation of Ti. After depassivation, the immersion potential dropped to the hydrogen evolution potential and a hydride layer was formed on the surface. The hydride layer dissolved continuously in the acidic solution. SEM observation showed that Ti wires dissolved almost uniformly in the early stage and that the dissolution then trace became irregular due to nonuniform growth of the hydride layer. Dissolution rate of a Ti wire was estimated almost accurately by resistometry.