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BIOMEDICAL, DENTAL MATERIALS AND ENGINEERING
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LABORATORY OF ADVANCED MATERIALS CHEMISTRY
DISSIMILAR MATERIALS INTERFACE ENGINEERING
LABORATORY

OTHER CORRESPONDING MEMBER

Assoc Prof. Dr. Hiroki Tamura

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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 polypyrrole (PPy) film doped by molybdophosphate (MoP) ions was successfully formed on the steel plate by electropolymerization from pyrrole monomers in aqueous solutions. MoP ions doped in the layer enhances the formation of passive oxide film on the steel-polypyrrole interface. The PPy-MoP composite film greatly decreases the corrosion rate of the steel plate to a level of the passive current in 3.5 wt% NaCl solutions at PH1.9 and 5.2 and keep the open circuit potential high enough for the passive region for a week.

(2) Monitoring of corrosion layer on zinc by Raman spectroscopy

Formation process of corrosion layer on zinc and zinc alloy covering steels formed in humidified atmosphere was monitored by Raman scattering spectroscopy under the in-situ condition. At the presence of NaCl, aqueous ZnCl₂ layer is at first formed by the electrochemical reactions of zinc dissolution and oxygen reduction in the water layer adsorbed from the humidified air. When the concentration of ZnCl₂ in the aqueous surface layer increases and reaches the saturation, simonkolleite begins to precipitate: $ZnCl_2 + 4Zn^{2+} + 8OH^- + H_2O \rightarrow ZnCl_2 \cdot [Zn(OH)_2]_4 \cdot H_2O$. The time periods to the formation of simonkolleite greatly depended on the composition of alloys. Addition of Al and Ni into zinc coatings delays the formation simonkolleite.

(3) Potential modulation reflectance of passive stainless steels

In order to estimate the physical properties of the passive oxide film on 304 stainless steel, AC potential modulation was applied to the passivated steel. The reflectance modulation response was compared with the current response (ie, impedance). The AC response suggested the passive film formed in acidic sulphate solution reveals n-type semiconductive characteristics. From the potential modulation reflectance spectra, the band gap, ie., absorption edge, is assumed to be about 3eV.

(4) Rust layer on weathering steels

On weathering steels, active and growable rust layer is occasionally formed. The conditions under which such active rust layer is formed has been examined. It was found that the active rust layer was formed in environment where dry period is extremely short and air-borne salt concentration is relatively high.

(5) Improvement of corrosion resistance of TiAl inter-metallic compound by coating of Al-Cr-Ni alloy from a molten salt electrolysis

A coating layer of Al-Cr-Ni alloy was cathodically formed at 333 K on the TiAl inter-metallic compound in an AlCl₃-EMIC ambient molten salt containing CrCl₂ and NiCl₂. Al-Cr-Ni alloy composition was controlled by potential pulse

method.

(6) Corrosion products on copper in humid air containing sulfur dioxide

Corrosion products formed on copper in air containing SO₂ have been investigated by using in situ IR-RAS. The growth-rate of the corrosion products, Chevrel's salt and sulfate, was low at the initial stage for the protection by oxide films and the rate increased after the degradation of the films. As the concentration of SO₂ decreased, Chevrel's salt decomposed mostly to SO₂ and partly changed to sulfate. This suggests that the variation in concentration of SO₂ in atmospheric environments causes increase in the ratio of sulfate to Chevrel's salt.

(7) Adsorption of MPSA and PEG on a copper electrode in perchloric acid

Adsorption of 3-mercapto, 1-propane sulfonic acid (MPSA) and polyethylene glycol (PEG) on copper in perchloric acids was investigated by using in situ surface-enhanced infrared absorption spectroscopy and cyclic voltammetry. The adsorption of both molecules to copper was confirmed and it was also elucidated that the adsorbed molecules tend to rise from the copper surface as potential shifts to cathodic region, and water molecules were removed from the surface in case of MPSA, on the other hand, they were brought close to the surface in case of PEG.

Other Activities

Prof. Ohtsuka and Dr. Ueda attended the 2004 Joint International Meeting of ECS and ECSJ, Hawaii, 3-8 Oct., 2004 and presented papers entitled by "Atmospheric Corrosion of Zinc and Zinc Alloy Using In-situ Raman Spectroscopy", "Co-deposition of Al-Cr and Al-Ni Alloys Using Potential Pulse Technique in Molten Salt", and "

Dr. Ueda attended the Galvatech '04, Chicago, 4-7 Apr., and a presented paper entitled by Corrosion Products on Zinc-coated Steels Detected by In-situ Raman Spectroscopy.

Presentations

Electrodeposition of Al Alloy by Constant Potential and Pulse Technique in AlCl_3 Molten Salt Containing CrCl_2 and NiCl_2 , H. Kigawa, M. Ueda, and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Sapporo, Jan., 2004.

Surface Enhanced Infrared Spectroscopy of 3-mercapto, 1-sulfuric Acid Adsorbed on Copper Electrode

M. Yasuda, T. Sasaki, M. Osawa and T. Ohtsuka

Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Sapporo, Feb., 2004.

Thin Layer Formation of Perovskite Type Oxide Powder by Electrophoretic Deposition, M. Kamiya, M. Ueda, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Sapporo, Feb., 2004.

Determination of Corrosion Products of Copper and Adsorbed Water in Humid Air Containing Sulfur Dioxide by in situ IR-RAS. Y. Horiguchi, T. Sasaki and T. Ohtsuka, The 2004 Joint Meeting of Hokkaido Section of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Corrosion Eng., Sapporo, Feb., 2004.

Electrodeposition of Al Alloy in EMIC Ambient Molten Salt, H. Ebe, M. Ueda, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Sapporo, Feb., 2004.

Investigation of Atmospheric Corrosion Products on Zinc-coated Steels Presented NaCl, M. Matsuda, M. Ueda, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Sapporo, Feb., 2004.

Co-deposition of Cr-Al and Ni-Al Alloy from AlCl_3 -NaCl-KCl Molten Salt, M. Ueda, H. Kigawa and T. Ohtsuka, Electrochemical Society Jpn., Yokohama, March, 2004.

Corrosion Products on Zinc-coated Steels Detected by In-situ Raman Spectroscopy, M. Ueda, M. Matsuda, and T. Ohtsuka, Galvatech'04, Chicago, Apr., 2004.

Rust Layers on Weathering Steels Exposed in Various Sites for 17 or 18 years, T. Ohtsuka, The 145th Symposium of Corrosion and Corrosion Protection – SUBI [Rust] Chemistry for New Paradigm on Corrosion Engineering of Steel Bridges, JSCE, June 2004, Tokyo.

Electrophoretic deposition Condition of Perovskite Type Oxide Powder for Thin Layer Formation, M. Ueda, M. Kamiya, and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Sapporo, July., 2004.

Al-Ni-Cr Alloy Co-electrodeposition in AlCl₃-EMIC Ambient Molten Salt by Pulse Technique, H. Ebe, M. Ueda, and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Sapporo, July., 2004.

Local Coating of Conducting Polymer Film by Aluminum Anodizing, Laser Irradiation, and Electrolytic Polymerization ; Y. Akiyama, M. Iida, M. Ueda, T. Kikuchi, M. Sakairi, and H. Takahashi : The Hokkaido Branch of Chem. Soc. Jpn. and Soc. Anal. Chem., Tomakomai, July, 2004.

Al Alloy Electrodeposition in AlCl₃-EMIC Ambient-temperature Molten Salt by Pulse Electrolysis, H. Ebe, M. Ueda, and T. Ohtsuka, The 110th Annual Meeting of Surf. Finish. Soc. Jpn., Matsushima, Sep., 2004.

Patterning of Polypyrrole Film by Aluminum Anodizing, Laser Irradiation, and Electrolytic Polymerization ; Y. Akiyama, T. Kikuchi, M. Ueda, M. Iida, M. Sakairi, and H. Takahashi : The 110th Annual Meeting of Surf. Finish. Soc. Jpn., Matsushima, Sep., 2004.

Fabrication of Microactuators by Aluminum Anodizing, Laser Irradiation, Polypyrrole Deposition ; Y. Akiyama, T. Kikuchi, M. Iida, M. Ueda, M. Sakairi, and H. Takahashi : 5th Intern. Symp. On Electrochemical Micro and Nano System Technologies, Tokyo, Sep., 2004

Prototype of Electrochemical Actuator by Aluminum Anodizing, Laser Irradiation, and Electrolytic Polymerization ; Y. Akiyama, T. Kikuchi, M. Iida, M. Ueda, M.

Sakairi, H. Takahashi :The 21th ARS (Anodizing Research Society, SFJ) Conf., Nara, Oct., 2004.

Effect of Variation in Gaseous Environments on Copper Corrosion

Y. Horiguchi, T. Sasaki and T. Ohtsuka

The 51st Discussion Meeting of Jpn. Corros. Eng., Nagoya, Sep., 2004.

Enhancement of electric conductivity of the rust layer on weathering steels by water adsorption, T. Ohtsuka, T. Komatsu and T. Sasaki, 2004 Joint meeting of ECS and ECSJ, Hawaii, Oct. 2004.

Atmospheric Corrosion of Zinc and Zinc Alloy Using In-situ Raman Spectroscopy, M. Ueda, M. Matsuda, and T. Ohtsuka, 2004 Joint meeting of ECS and ECSJ, Hawaii, Oct. 2004.

Co-deposition of Al-Cr and Al-Ni Alloys Using Potential Pulse Technique in Molten Salt, M. Ueda, H. Kigawa and T. Ohtsuka, 2004 Joint meeting of ECS and ECSJ, Hawaii, Oct. 2004.

Consideration about the Definition of Molten Salt and Ionic Liquid, K. Ui, M. Ueda, R. Hagiwara, and M. Mizuhata, Molten Salt Committee of the Electrochemical Society of Japan, Oct. 2004, Osaka

Application of Ionic Liquid for Aluminum Alloy Deposition, M. Ueda, 1st meeting in Low Temperature Molten salt and Ionic Liquid, Kyoto, Nov. 2004.

Investigation of Al Alloy Electrodeposition in AlCl₃-EMIC Ambient Molten Salt, M. Ueda, H. Ebe, and T. Ohtsuka, Kyoto, Nov. 2004.

Impedance Characteristics of Rust Layer and Its Interpretation, T. Ohtsuka, The 149th Symposium on Corrosion and Corrosion Protection – Symposium on Electrochemical Impedance Spectroscopy, JSCE, Dec. 2004, Tokyo.

Facilities and Capabilities

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light.

Potential Modulation Reflectance: Wavelength region from 350 to 800 nm.

Raman Scattering Spectrometer: JASCO R-800T, triple type of spectrometer equipped with an Argon gas laser of 2W power.

FT-IR Spectrometer: JASCO FT/IR 550 equipped with MCT detector for in-situ measurement of corrosion layers on metals.

QCM system for in-situ gravimetry of surface layer on metals.

Electrochemical AC Impedance: NF Circuit Design 5020 FRA equipped with a specially designed potentiostat.

Spectrophotometer: JASCO V-520 in a wavelength region from 200 to 900 nm.

Electrochemistry apparatuses.

Optical Microscopy

Electrochemical Corrosion-Rate Monitor System.

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The research activity of the laboratory still continues to be directed towards a better understanding of the interfacial properties of metal and semiconductor electrodes in relation to the interfacial electrochemistry involving adsorption, corrosion, passivation, anodic oxidation, hydrogen adsorption / absorption, and surface finishing. Current topics on research are as follows:

(1) Nano-scratching in Solution to the Ta (100) Surface Subjected to Anodic Oxidation

A single-crystal Ta (100) disc plate with a diameter of 10 mm and a thickness of 2mm was used for experiments. The Ta specimen was mechanically polished with diamond paste, ultrasonically washed in ethanol and finally electropolished in a mixed solution of 90 % H₂SO₄ and 10 % HF. The Ta specimen was galvanostatically oxidized up to 5 V (SHE) in pH 8.4 borate solution and then kept at 5 V. The nano-scratching in solution for the Ta specimen surface kept at 5 V and nano-scratching in air after anodic oxidation were performed by using a conical diamond tip with an angle of 90° under a constant normal force of $F_N = 300 \mu\text{N}$ at various scratching rate of $v_s = 0.2 - 1.0 \mu\text{m s}^{-1}$ between lateral distance of 2 μm . Stick-slip phenomena were always observed during nano-scratching in solution and

became more significant at lower scratching rate. In contrast, no significant stick-slip phenomena were observed at any scratching rates during nano-scratching in air after anodic oxidation. The AFM image of the groove produced with nano-scratching in solution has indicated that debris is locally accumulated at the moving front of the diamond tip during scratching, which may be reflected by the stick-slip phenomena. The friction coefficient ($\mu' = 2.0 - 1.5$) obtained with nano-scratching in solution tended to decrease as the scratching rate increased, while that ($\mu' = 0.25$) obtained with nano-scratching in air was almost independent of the scratching rate.

(2) Current Transients of Passive Iron during Micro-indentation in Solution

A polycrystalline iron plate (1.2 cm x 1.2 cm x 0.2 cm) with a purity of above 99.99% was used for experiments. The iron specimen was mechanically polished with a diamond paste (3 μ m) and ultrasonically washed in ethanol. The electrolytes were pH 8.4 borate buffer solutions with and without 5×10^{-3} M sodium sulfate, which were deaerated with purified argon gas during experiments. A conical diamond indenter with an including angle of about 110° was employed for micro-indentation. For micro-indentation in solution, the diamond indenter attached to a force sensor was normally moved with a piezoelectric-driving system to the passive iron surface kept at constant potential. Two different indentation modes were employed; one was a sweep indentation at a rate of $10 \mu\text{m s}^{-1}$, the other was a step indentation up to a maximum depth of 60 μm . The maximum load corresponding to the maximum depth was 0.5 N.

For both indentation modes, the sharp anodic current peaks appeared at the initial stage of loading, i.e., at the moment when the indenter penetrated into the passive iron surface. The sharp anodic current peaks also emerged at the final stage of unloading, i.e., at the moment when the indenter was removed from the passive iron surface. The addition of sulfate in solution enhanced the anodic current peaks. The anodic current peaks were associated with break down and repair of passive film.

(3) Measurement of Stress Changes during Anodic Oxidation and Cathodic Reduction of the Cu/Cu₂O Multi-layer Film

The changes in stress of the Cu/Cu₂O multi-layer film during anodic oxidation and cathodic reduction in pH 8.4 borate solution were measured by a bending beam method. The stress of the multi-layer film increased to the compressive

direction during potentiostatic oxidation in the passive potential region, while the stress of the pure copper film increased to the tensile direction. EQCM analysis has indicated that the difference in direction of stress changes between multi-layer film and pure copper film is originated from the difference in transference numbers of Cu^{2+} and O^{2-} during anodic oxidation.

The compressive stress was generated during galvanostatic reduction of the multi-layer film. However, the stress changed rapidly to the tensile direction at the final stage of cathodic reduction. EQCM analysis has indicated that water molecules produced by the cathodic reduction remained in the surface layer and released from the surface layer at the final stage. The generation of compressive stress during cathodic reduction and the changes in stress to the tensile direction may be ascribed to the remaining and release of water molecules.

(4) Application of Resistometry to Corrosion Monitoring of Ti.

Resistometry equipment was improved to reduce influence of temperature fluctuation to resistance of metals which limited the accuracy of measurement. The principle was the use of a couple of metal specimens; one is the reference resistance protected from corrodible environment and the another is used as corroding sample exposed to environment. Electric resistance of corroding sample was measured as a relative value to the referenced resistance. Because both specimens have same temperature dependence of resistance, fluctuation of resistance on temperature shift is considerably reduced. In the experiments Ti wire of 0.1 mm diameter and 140 mm in length was immersed in acidic solution containing H_2SO_4 and HCl at various concentration. The solution was deaerated using deoxidizer and its temperature was elevated from room temperature to 353 K to simulate the underground environment for high radiation-level nuclear waste container. In $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.1 \text{ mol dm}^{-3} \text{ HCl}$ solution Ti showed depassivation, i.e., resistance began to increase and immersion potential dropped lower than hydrogen evolution potential after some induction period. Ti continuously dissolved accompanying with formation of surface hydride layer. Addition of HCl to solution considerably lowered the H_2SO_4 concentration which was necessary to cause depassivation. Dissolution rate of Ti was evaluated to be $0.15 - 0.4 \text{ nm s}^{-1}$ from the resistance change.

(5) Formation of Small Metal Structures and Patterns using Electrochemical Methods

To form small metal object and metal pattern some methods were examined. A thin glass tube less than 1 mm in inner diameter containing Cu wire acted as anode and electrolyte solution containing CuSO_4 and H_2SO_4 was pressed to metal plate acted as cathode. This small electrochemical cell was then electrolyzed to dissolve Cu anode and deposit Cu on Cathode within the glass tube. The shape of resultant Cu deposition was evaluated as a function of current density, cell voltage, composition of solution, and pattern for pulse polarization. Three -dimensional metal object was formed for demonstration by repeating local deposition with this small cell. In another method sharp tip of Pt wire electrode was approached to Al film formed by magnetron sputter deposition on glass plate and then cathodically polarized. This caused local alkalization around Pt tip enough to dissolve the Al film surface. Small holes less than 0.1 mm in diameter and square dissolution pattern less than 1 mm were formed by moving the Pt electrode during polarization.

(6) Computer Simulation of Metal Deposition Process

Analysis of behavior of adatom on metals as an elemental process of metal deposition is important to control the deposition form in electro- or electroless deposition of metals. Semiempirical molecular orbital method was applied to analyze the surface diffusion process of Zn adatom on Zn surface. Cluster model or periodical cell model was used to construct metal surface and the total energy of the system was calculated as a function of position of adatom on the surface to obtain the energy map using Gaussian program. From the energy maps calculated for terrace, step and kink, which were typically used to explain the epitaxial growth in metal deposition, surface diffusion energy of adatom in these situations was estimated. Although experimental value of them for zinc was not found in the literature, they were in similar order comparing with the values of tungsten measured in vacuum condition.

(7) Passive Film on Shape Memory NiTi Alloy

Shape memory NiTi alloy was polarized anodically in methanolic or aqueous H_2SO_4 solution to remove or to form oxide films on the surface. Anodic polarization of NiTi at potentials higher than 2 V in methanolic 3 mol dm^{-3} H_2SO_4 solution at 263 K gave a limiting current and produced a smooth surface. These

conditions showed the best electropolishing results for $0.1 \text{ mol dm}^{-3} \leq C_{\text{H}_2\text{SO}_4} \leq 7 \text{ mol dm}^{-3}$. The passivity of NiTi was better than that of Ni but poorer than that of Ti in aqueous $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution. XPS analysis revealed that TiO_2 -based oxide film formed on NiTi and its thickness and composition depended on film the formation potential. The semiconductive properties of the oxide film were investigated by EIS. The permittivity or donor density of the film was similar to that of anodic oxide film on pure Ti. The dependence of the inverse of capacitance, C^{-1} , on the potential was explained by using the band structure model.

(8) Unique Electrochemical Performance of Microelectrode Vibrating Ultrasonically

Shear-force measurement in scanning electrochemical microscopy (SECM) is effective to improve resolution of SECM image as well as to control the distance between the SECM probe microelectrode and specimen surface. For application of shear-force sensing SECM, a microelectrode was vibrated ultrasonically in a lateral direction. Voltammetry of the microelectrode showed some unique electrochemical phenomena coupled with hydrodynamics. Vibration of the microelectrode increased the current flowing through the microelectrode at definite frequencies. At the definite frequencies, the approach of the vibrating microelectrode to an insulator surface also increased the current with decreasing distance in the vicinity of the insulator, phenomena that were ascribed to deformation of the diffusion layer on the electrode due to motion of the solution.

Other Activities

In July, Prof. M. Seo was invited to the 8th Ultra-Steel Workshop, NIMS, Tsukuba, Jpn. and presented the lecture entitled “Mechanical Properties of the Single-Crystal Iron Surfaces Kept at Passive State in Solution”. In August, Assoc. Prof. K. Azumi and Prof. M. Seo participated in International Symposium on Corrosion and Protection of Marine Structures in Honor of the Late Professor Toshihei Misawa, Muroran, Jpn. and presented the lecture entitled “Hydrogen Absorption Monitoring of Sputter-deposited Ti Film in Sea Water”.

In September, Prof. M. Seo participated in the 55th Annual Meeting of the International Society of Electrochemistry, Thessaloniki, Greece and presented the Keynote lecture entitled “Nano-mechano-electrochemical Properties of Passive Metal Surfaces Evaluated by Nano-indentation and Nano-scratching”. Prof. M. Seo, Assoc.

Prof. K. Azumi, and Dr. K. Fushimi participated in the 5th International Symposium on Electrochemical Micro and Nano System Technologies (EMT2004) and presented the lectures entitled “Local formation of porous layer on InP by an electrochemical etching combined with a scratching”, “Micro-electroforming of Cu using thin-tube electrochemical cell”, and ”Performance of ultrasonically vibrated microelectrode”, respectively.

In October, Prof. M. Seo participated in the 206 th ECS Meeting, Honolulu, USA, to present the lecture entitled “ Morphology of Porous Layer Formed Locally on n-InP (001) by anodic polarization in HCl after Scratching” and received the 2004 ECS Fellow Award for nanoscale *in-situ* characterization of metals and alloys.

Presentation

M. Yamazaki and M. Seo; Changes in Surface Stress of Gold Electrode during Cu-UPD, The 2004 Joint Meeting of Hokkaido Section of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Corrosion Eng., Sapporo, Feb. 2-4, 2004.

M. Hagioi and M. Seo; Electrochemical Characteristics of the Cu/Cu₂O Multi-layer Film, *ibid.*

T. Yamaya and M. Seo; Local Formation of Porous layer on n-type InP surface by Scratching, *ibid.*

K. Iokibe, K. Azumi, and M. Seo; Determination of Parameters for Semiempirical MO Calculation using Genetic Algorithm; *ibid.*

D. Kawamata, and M. Seo; Measurement of Friction Coefficient of Single-Crystal Ta (100) Surface by Nano-scratching, *ibid.*

A. Kanada, K. Azumi, and M. Seo; Attempt of TiN formation on Ti using Glow discharge treatment in Nitrogen Gas, *ibid.*

K. Okamoto, K. Azumi, and M. Seo; Application of Temperature-Compensated

Resistometry on Corrosion Monitoring, *ibid.*

K. Nishimura, K. Azumi, and M. Seo; Role of Zn Layer formed by Zincate Pretreatment in Electroless Ni Plating on Aluminum, *ibid.*

M. Hagioi and M. Seo; Electrodeposition and Cathodic Reduction of the Cu/Cu₂O Multi-layer Film, The 107th Annual Meeting of Surf. Finish. Soc. Jpn., Tokyo, Mar. 15-17, 2004.

D. Kawamata and M. Seo; Nano-scratching to the Single-Crystal Ta (100) Surface Subjected to Anodic Oxidation, *ibid.*

K. Iokibe, K. Azumi, and M. Seo; Analysis of Zn-Adatom Diffusion on Zn Surface using MO method, *ibid.*

K. Azumi, K. Nishimura, and M. Seo; Control of Ni Nucleation at the Initial stage of Electroless Ni Plating on Aluminum, *ibid.*

K. Fushimi, M. Ueda, T. Ohtsuka, M. Seo, A.W. Hassel, and M. Stratmann; Analysis of Semiconductive Property of Passive NiTi, The 2004 Annual Meeting of Jpn. Soc. Corros. Eng., Tokyo, Apr. 26-28, 2004.

K. Azumi, K. Okamoto, and M. Seo; Monitoring of Ti Corrosion in High-temperature Aqueous Solution using Resistometry, *ibid.*

M. Seo, and M. Hagioi; Preparation and Cathodic Reduction of the Electrodeposited Cu / Cu₂O multi-layer Film, *ibid.*

K. Azumi and M. Seo; Corrosion Behavior of Titanium in Non-oxidative High-temperature Aqueous Environment, The 71st Meeting of the Electrochem. Soc. Jpn., Yokohama, Mar. 24-26, 2004.

M. Seo and M. Chiba; Mechanical Properties of the Single-Crystal Iron Surfaces Kept at Passive State in Solution, 8th. Ultra-Steel Workshop, NIMS, Tsukuba, July 21-22,

2004.

K. Azumi and M. Seo; Hydrogen Absorption Monitoring of Sputter-deposited Ti Film in Sea Water, Inter.Symp. Corrosion and Protection of Marine Structures (in Honor of the Late Professor Toshihei Misawa), Muroran, Aug. 30-31, 2004.

M. Seo and M. Chiba; Cyclic Nano-indentation to the Passive Surface in Dichromate Solution, The 51st Conf. on Materials and Environments, Nagoya, Sept. 8-10, 2004.

M. Hagioi and M. Seo; Measurement of Stress Change during Cathodic Reduction of the Cu/Cu₂O Multi-layer Film, *ibid.*

M. Seo and M. Chiba; Nano-mechano-electrochemical Properties of Passive Metal Surfaces Evaluated by Nano-indentation and Nano-scratching, 55th Annual Meeting of the International Society of Electrochemistry, Thessaloniki, Greece, Sept. 19-24, 2004(Keynote lecture)

M. Seo and T. Yamaya; Local formation of porous layer on InP by an electrochemical etching combined with a scratching, 5th International Symposium on Electrochemical Micro & Nano System Technologies (EMT2004), Tokyo, Sept.29-Oct. 1, 2004 (Invited Lecture).

K. Azumi, N. Munakata, and M. Seo; Micro-electroforming of Cu using thin-tube electrochemical cell, *ibid.*

K. Fushimi, K. Azumi, and M. Seo; Performance of ultrasonically vibrated microelectrode, *ibid.*

M. Seo; Morphology of Porous Layer Formed Locally on n-InP (001) by anodic polarization in HCl after Scratching, The 206 th ECS Meeting, Honolulu, USA, Oct.3-8, 2004.

M. Hagioi; Analyses of Changes in Mass and Stress during Anodic Oxidation and Cathodic reduction of the Cu Film and Cu/Cu₂O Multi-layer Film, Corrosion Dream

2004 Seminar of Corrosion Division, The Electrochem. Soc. Jpn., Sapporo, Oct. 29,
2004.

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Equipments

Atomic Force Microscope

Confocal Scanning Laser Microscope

Pulsed Nd-YAG Laser Patterning System

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) Fabrication of 3 electrodes micro-reactor by anodizing, laser irradiation and electroplating

Porous anodic oxide film formed aluminum specimens were irradiated with pulsed Nd-YAG laser to produce through-holes with 300 μm diameter, channels with 300 μm width, and electrode chambers with 0.4 mm^3 volume on the surface, and Au layer was deposited on the surface of the chamber. Electrochemical reactors were fabricated by attaching the surface-modified specimen to another one via a Teflon sheet, and evaluated on the electrochemical performance using a $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ solution system. A cyclic voltamogram showed redox peaks of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ ions, indicating linear dependence of peak current on square root of scanning rate and on cube root of flow rate.

(2) Study on initial stage of localized corrosion in artificial pit formed on zinc-coated steels by photon rupture

Zinc alloy coated steel specimens, which coated layers thickness are about 20 μm , covered with nitrocellulose film were irradiated with focused pulsed Nd-YAG laser beam for long time to form artificial small pit in 0.5 kmol m^{-3} H_3BO_3 - 0.05 kmol m^{-3} $\text{Na}_2\text{B}_4\text{O}_7$ (pH = 7.4) with chloride ions. It took about $t_r = 2$ s to remove zinc coated layer by laser irradiation. The rest potential changed to noble direction just after laser was irradiated, and then returned to previous value at periods of $t_r < 2$ s, during zinc covered on the steel. However, after 2 s of t_r , the steel substrate was exposed to the solution, the rest potential move to positive direction just after laser was irradiated and then returned to previous value. These rest potential fluctuation difference may be due to the galvanic reaction between zinc coated layer and steel substrate.

(3) Effect of anodic oxide film structure on galvanic corrosion of aluminum alloys in Cl⁻ containing solutions

Aluminum alloy specimens on which porous and barrier type oxide films were formed, were immersed in Cl⁻ ion containing solutions to study effects of film structure on galvanic corrosion, by monitoring rest-potential and corrosion current

between sample and Pt-counter electrode. Oxide film microstructure affected the incubation time for localized corrosion. Corrosion impedance was also measured by FFT and decreased after localized corrosion started.

(4) Study on initial stage of localized corrosion of titanium in quasi-biological solutions by photon rupture method.

Anodized titanium sheets were irradiated with focused pulsed Nd-YAG laser beam in quasi-biological solutions with and without chloride ions. In both solutions, oxide films are reformed under constant potentials after removal of the anodic oxide film by photon rupture. The oxide film formation rates were faster than that expected from the inverse logarithmic law, according to Cabrera-Mott theory. The current increased with increasing applied potential and chloride ions concentration.

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

DC-etched aluminum specimens were coated with SiO₂ films by a sol-gel electrophoretic method, and then anodized galvanostatically in a boric acid solution. Anodizing of SiO₂ film-coated specimens lead to the formation of anodic oxide films consisting of an outer Al-Si composite oxide layer and an inner alumina layer(?). Parallel capacitance of anodic oxide films obtained thus was larger than that obtained on specimens without any coating, and this tendency became more remarkable as the film formation potential increased.

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

Aluminum specimens covered with porous type anodic oxide films were irradiated with a pulsed Nd-YAG laser to remove the oxide film locally, and gold thin layer was deposited on aluminum substrate exposed to the solution by laser irradiation. Then, the specimen was immersed in NaOH solution to dissolve anodic oxide films and the metal substrate. Poly-pyrrole films were deposited on a one side of the gold layer from pyrrole / sodium dodecyl-benzene sulfonate solutions. The gold / poly-pyrrole structure showed swinging motion by repeating anodic / cathodic polarization.

(7) Formation of niobium anodic oxide films

Niobium specimens were anodized in H_3PO_4 solutions galvanostatically up to $E_a = 20 - 100$ V, and then the potential of the specimens was kept at E_a for 2 hrs. Anodic oxide films were characterized by SEM, CSLM, GDS, AFM and electrochemical impedance measurements as functions of E_a , c. d. of galvanostatic anodizing, temperature, and H_3PO_4 concentration. There were many imperfections in anodic oxide films, and the number of imperfections strongly depended on anodizing conditions.

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

Aluminum foils covered with thin barrier type anodic oxide films were set at the bottom of an electrochemical cell on the stage of atomic force microscope (AFM) and then solutions containing small particles of acrylic acid / melamine resin were added in the cell. Under anodic polarization, the specimen was scratched by a diamond probe of AFM. Deposition of resin was observed at the scratched area.

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

Copper deposition at selected area on aluminum alloy covered with anodic oxide films were attempted by laser irradiation and electro-plating. Formation of relatively thick porous type anodic oxide films and pore-sealing in boiling water were essential to avoid copper deposition through imperfections at area without laser irradiation.

In January, Dr. T. Kikuchi joined LIMSA as an instructor. In March, Mr. Z. Kato received the engineering doctor degree, and left for Sendai to continue his research life with Prof. K. Hashimoto.

In April, Assoc. Prof. Sakairi attended "Galvatech '04" in Chicago to present a paper entitled "Initial Stage of Localized Corrosion on Zn-5mass% Al Coated Steels with Photon Rupture Method in Cl^- Solutions". After the conference, he visited Dr. Ueno, and Mr. Ono at Chemi-Con Materials Corporation.

In May, Prof. Takahashi attended "FSISE 2004" held at Guangzhu in China to present a paper entitled "Anodizing of Aluminum Covered with Ta_2O_5 films by MOCVD - For the Development of Novel Aluminum Electrolytic Capacitors-.

After the symposium, he visited Prof. Z. Jiang at Fudan Univ., Shanghai, China and talked on the micro-patterning of aluminum by laser irradiation and electrochemical technique.

In August, International Symposium of Corrosion and Prevention for Marine Structures - in Honor of the Late Professor Toshihei Misawa- was held in Muroran. Dr. Sakairi presented a paper entitled "The Initial Stage of Pitting Corrosion on Coated Steels Investigated by Photon Rupture in Chloride Containing Solutions".

In September, Dr. Sakairi attended "55th ISE annual meeting" in Tesseloniki, Greece, to present a paper entitled "Effect of Ion Concentration on Initial Stage of Artificial Pitting Corrosion on Zn Alloy Coated Steels by Photon Rupture Method". Prof. Takahashi, Dr. Kikuchi and Mr. Nagahara attended 5th International Symposium on Electrochemical Micro & Nano System Technologies (EMT 2004) held at Tokyo. At the poster session, Dr. Kikuch presented a paper entitled "Fabrication of Micro-actuators by Aluminum anodizing, Laser Irradiation, and Polypyrrole Deposition", and Mr. Nagahara presented a paper on "Mechanism of Formation of Anodic Oxide films and Growth of Sunflower-Like Imperfections in Anodic Oxide Films on Niobium".

In October, Dr. Sakairi and Prof. Takahashi attended "2004 Joint international meeting of ECS " in Honolulu. Dr. Sakairi present papers entitled "Electrochemical Noise Study on Galvanic Corrosion of Anodized Aluminum in Chloride Environments" and "Fabrication of Electrochemical Micro-reactor by Photon Rupture Method and Electrochemistry". Prof. Takahashi presented papers entitled " Blister and Pit Formation during Cathodic Polarization of Aluminum Covered with Anodic Oxide Films" and " Formation of Al-(Ta, Nb, Si, Ti) Composite Oxide Films on Aluminum - Development of Aluminum Electrolytic Capacitors with High Capacitance -".

In December, Dr. Sakairi and Prof. Takahashi visited Prof. S.-G. Park at Chungbuk National University, Cheongju, Korea. On mini-symposium, Dr. Sakairi presented a paper entitled "Fabrication of Electrochemical Micro-reactor on Aluminum by Photon Rupture", and Prof. Takahashi talked on "Formation of Al-(Si, Ta) Composite Oxide Films on Aluminum by the Combination of MOCVD and Electrophoretic Sol-Gel Coating with Anodizing"

Foreign scientists visited LIMSA in 2004 were Prof. Z. Jiang, Fudan Univ. between July 8 – 12, Prof. K. -B. Kim, Yonsei Univ., Seoul, Korea between Aug. 4 - 8,

Prof. S. -G. Park, Chungbuk National Univ., Korea between Aug. 4 – 7, Dr. Z. Zhu, Non-Ferrous Metal Research Inst., Beijing, China between Sept. 2 – 6.

Presentations

Study on Corrosion and Surface Finishing by Laser Irradiation and Electrochemistry ; M. Sakairi : Research Group of Interface Control Engineering seminar : Sapporo, Jan., 2004.

Influence of Heat Treatment on Anodic Oxide Films on Tantalum ; S. Nishikawa, K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda : The Winter Joint Meeting of the Hokkaido Secs. Of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan., 2004

Formation of Al-Si Composite Oxide Films on Aluminum by Electrophoretic Sol-gel Method and Anodizing ; M. Sunada, M. Sakairi, S. Hirai, K. Watanabe, and H. Takahashi : *ibid.*

Influence of Oxidation Conditions on Forming Imperfections in Anodic Oxide Films on Niobium ; K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda : The Joint Meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Feb., 2004

Change in Dielectric Properties of Anodic Oxide Films on Aluminum with Heat Treatment ; M. Yamada, M. Sakairi, H. Takahashi, K. Nogami, and H. Uchi : *ibid.*

SCLM-Analysis of Inhomogeneity in the Thickness of Aluminum Anodic Oxide Films ; Y. Ogawa, N. Katayama, M. Sakairi, and H. Takahashi : *ibid.*

Electrochemical Micro-cell Formed on Anodized Aluminum and its CV Behavior ; M. Yamada, M. Sakairi, and H. Takahashi : The Hokkaido Secs. of Chem. Soc. Jpn. and

Soc. Anal. Chem., Sapporo, Feb., 2004.

Dielectric Properties of Composite Oxide Films Formed on Etched-Al Foil by MOCVD / Anodizing ; E. Sakata, M. Sakairi, and H. Takahashi : *ibid.*

Micro-structure of Anodic Oxide Films by Ultra Micro-tormy ; M. Sakairi : The 109th Annual Meeting of Surf. Finish. Soc. Jpn., Tokyo, Mar., 2004.

Anodizing of Aluminum Coated SiO₂ by Electrophoretic Sol-gel Method ; M. Sunada, M. Sakairi, S. Hirai, K. Watanabe, and H. Takahashi : *ibid.*

Fabrication of Electrochemical Micro-cell by Laser Irradiation and its Polarization Behavior ; M. Yamada, M. Sakairi, and H. Takahashi : The 71th Annual Meeting of the Electrochem. Soc. of Jpn. Yokohama. Mar., 2004.

Current Dependence of Structure and Dielectric Properties of Anodic Oxide Films on Niobium ; K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda : *ibid.*

Initial Stage of Localized Corrosion on Zn-5mass% Al Coated Steels with Photon Rupture Method in Cl⁻ Solutions ; M. Sakairi, K. Itabashi, and H. Takahashi : Galvatech '04, Chicago, April, 2004.

Effect of Anion Concentration on Localized Corrosion on Zn-Alloy Coated Steels by Photon Rupture ; M. Sakairi, Y. Uchida, K. Itabashi, and H. Takahashi : Zairyo-to-Kankyo 2004, Tokyo, May, 2004.

Anodizing of Aluminum Covered with Ta₂O₅ Films by MOCVD – For the Development of Novel Aluminum Electrolytic Capacitors - ; E. Sakata, M. Sakairi, H. Takahashi, and S. Nagata : FSISE 2004, Guangzhu, China, May, 2004

Development of Three-dimensional Microstructure Fabrication Method by Laser irradiation and Anodizing ; T. Kikuchi, M. Sakairi, and H. Takahashi : 6th Symposium

on Interdisciplinary Research on 21 Century, Sapporo, June, 2004

Fabrication of Three-dimensional Microstructure by Aluminum Anodizing, Laser Irradiation, and Electrochemical Technique ; H. Takahashi : 74th Meeting of Jpn. Inst. Of Light Metals, Tokyo, July, 2004

Effect of Oxide Film Structure on Galvanic Corrosion of Al in NaCl solutions ; Y. Shimoyama, M. Sakairi, and H. Takahashi : The Summer Joint Meeting of the Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, July, 2004.

Initial Stage of Localized Corrosion on Zn Coated Steels with Photon Rupture Method - Effect of Zn ions- ; Y. Uchida, M. Sakairi, and H. Takahashi : *ibid.*

Local Coating of Conducting Polymer Film by Aluminum Anodizing, Laser Irradiation, and Electrolytic Polymerization ; Y. Akiyama, M. Iida, M. Ueda, T. Kikuchi, M. Sakairi, and H. Takahashi : The Hokkaido Secs. of Chem. Soc. Jpn. and Soc. Anal. Chem., Tomakomai, July, 2004.

In-situ Atomic Force Microscopic Observation of Aluminum Covered with Anodic Oxide Films during Cathodic Polarization ; S. Kurokawa, Z. Kato, M. Sakairi, and H. Takahashi : *ibid.*

Micro-machining of Aluminum by Laser Irradiation and Electrochemical Technique ; T. Kikuchi, M. Sakairi, H. Takahashi, and T. Maruko : *ibid.*

The Initial Stage of Pitting Corrosion on Coated Steels Investigated by Photon Rupture in Chloride Containing Solutions ; M. Sakairi, K. Itabashi, Y. Uchida, and H. Takahashi : International Symposium of Corrosion and Prevention for Marine Structures - in Honor of the Late Professor Toshihei Misawa, Muroran, Aug., 2004.

Cathodic Polarization of Aluminum Covered with Anodic Oxide Films in Neutral Solutions – In-situ AFM Observation of Blister and Pit Formation - ; S. Kurokawa, Z. kato, M. Sakairi, and H. Takahashi : 2004 Annual Meeting of Jpn. Soc. Corrs. Eng.,

Nagoya, Sep., 2004

Effect of Oxide Film Structure on Galvanic Corrosion of Al ; Y. Shimoyama, M. Sakairi, and H. Takahashi : *ibid.*

Localized Corrosion of Zinc Coated Steel by Photon Rupture Method – Effect of Zn Ion Concentration - ; Y. Uchida, M. Sakairi, and H. Takahashi : *ibid.*

Three-electrode Type Micro-electrochemical Cell Formed on Anodized Aluminum and its CV Behavior ; M. Yamada, M. Sakairi, and H. Takahashi : The 110th Annual Meeting of Surf. Finish. Soc. Jpn., Matsushima, Sep., 2004.

Patterning of Polypyrrole Film by Aluminum Anodizing, Laser Irradiation, and Electrolytic Polymerization ; Y. Akiyama, T. Kikuchi, M. Ueda, M. Iida, M. Sakairi, and H. Takahashi : *ibid.*

Formation of Aluminum Coated SiO₂ by Electrophoretic Sol-gel Method ; M. Sunada, M. Sakairi, S. Hirai, K. Watanabe, and H. Takahashi : *ibid.*

Cathodic Polarization of Anodized Niobium in a Neutral Solution ; K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda : *ibid.*

Development of Surface Micromachining Method with Anodizing / Laser Irradiation / Electro-etching ; T. Kikuchi, M. Sakairi, H. Takahashi, and T. Maruko : *ibid.*

Effect of Ion Concentration on Initial Stage of Artificial Pitting Corrosion on Zn Alloy Coated Steels by Photon Rupture Method ; M. Sakairi, Y. Uchida, K. Itabashi, and H. Takahashi : 55th ISE annual meeting, Tsaloniki, Sep., 2004 .

Initial Stage of Localized Corrosion on Zinc Alloy Coated Steels by Photon Rupture Method ; M. Sakairi, Y. Uchida, K. Itabashi, and H. Takahashi : The 144th Fall Meeting of ISIJ, Akita, Sep., 2004.

Spectroscopic and Electron Microscopic Characterization of Metal-oxide Nanostructures Formed by Anodizing of Sputtered Valve-metal Bilayers in Citric Acid Electrolytes ; A. Mozalev, M. Sakairi, and H. Takahashi : 13th European Microscopy Congress, Sep., 2004

Mechanism of Formation and Growth of Sunflower-like Imperfections in Anodic Oxide Films on Niobium ; K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda : 5th Intern. Symp. On Electrochemical Micro and Nano System Technologies, Tokyo, Sep., 2004

Fabrication of Microactuators by Aluminum Anodizing, Laser Irradiation, Polypyrrole Deposition ; Y. Akiyama, T. Kikuchi, M. Iida, M. Ueda, M. Sakai, and H. Takahashi : *ibid.*

Electrochemical Noise Study on Galvanic Corrosion of Anodized Aluminum in Chloride Environments ; M. Sakairi, Y. Shimoyama, and H. Takahashi : 2004 Joint international meeting of ECS and ECSJ, Honolulu, Oct., 2004.

Fabrication of Electrochemical Micro-reactor by Photon Rupture Method and Electrochemical Technique ; M. Sakairi, M. Yamada and H. Takahashi : *ibid.*

Blister and Pit Formation during Cathodic Polarization of Aluminum Covered with Anodic Oxide Films – In-situ AFM Observation - ; S. Kurokawa, Z. Kato, T. Kikuchi, M. Sakairi, and H. Takahashi : *ibid.*

Formation of Al-(Ta, Nb, Si, Ti) Composite Oxide Films on Aluminum – Development of Aluminum Electrolytic Capacitors with High Capacitance - ; E. Sakata, M. Sunada, K. Watanabe, T. Kikuchi, M. Sakairi, and H. Takahashi : *ibid.*

Galvanic Corrosion of Anodized Aluminum ; Y. Shimoyama : Corrosion Dream 2004, Sapporo, Oct., 2004.

Initial Stage of Localized Corrosion on Coated Steels by Photon Rupture Method ; Y.

Uchida : ibid.

Development of Electrochemical Micro-cell using Anodic Oxide Films ; M. Sakairi, M. Yamada, T. Kikuchi, and H. Takahashi : The 21th ARS (Anodizing Research Society, SFJ) Conf., Nara, Oct., 2004.

Influence of Anodic Oxide Film Structure on Galvanic Corrosion of Al in NaCl Solutions ; Y. Shimoyama, M. Sakairi, and H. Takahashi : ibid.

Analysis of Initial Stage of Localized Corrosion on 55 mass% Al-Zn Coated Steels by Photon Rupture Method ; Y. Uchida, M. Sakairi, and H. Takahashi : ibid.

Influence of Electrolytic Conditions on Structure and Dielectric Properties of Anodic Oxide Films on Niobium ; K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda : ibid.

Prototype of Electrochemical Actuator by Aluminum Anodizing, Laser Irradiation, and Electrolytic Polymerization ; Y. Akiyama, T. Kikuchi, M. Iida, M. Ueda, M. Sakairi, H. Takahashi : ibid.

Cathodic Polarization of Aluminum in Neutral Solutions – In-situ AFM Observation of Blister and Pit Formation - ; S. Kurokawa, Z. Kato, M. Sakairi, and H. Takahashi : ibid.

Formation Process of Composite Oxide Films by MOCVD / Anodizing and Electrophoretic Sol-gel Coating / Anodizing ; E. Sakata, M. Sunada, K. Watanabe, T. Kikuchi, M. Sakairi, and H. Takahashi : ibid.

Fabrication of Electrochemical Micro-reactor on Aluminum by Photon Rupture ; M. Sakairi, M. Yamada, and H. Takahashi : Innovation and Development of Novel Capacitors, Chungbuk, Dec., 2004

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

(2) Development of functionally graded dental implant

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

microscope(XSAM) with unstained specimens.

(3) Modifications of carbon nanotubes for biological applications

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

(4) Development of FRP esthetic orthodontic wire

To realize the esthetic, transparent orthodontic wire the FRP wires of the diameter 0.5mm with the multiple fiber structure has been fabricated by either drawing of fiber-polymer complex at 250C or photopolymerization method. Biocompatible $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (CPSA) glass fibers of 8-20 μm in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bis-GMA. The improvement has been done to obtain the adequate flexural strength and higher torque. FRP wire shows the sufficient flexural strength and a very good elastic recovery. The dependence of Young's modulus and flexural stress on fiber fraction obeys very well the rule of mixture. This FRP wire can cover the range of the strength corresponding to the conventional metal orthodontic wires from Ni-Ti used in the initial stage of

orthodontic treatments to Co-Cr used in the last stage by changing the volume ratio of glass fibers with the same external diameter. FRP wire can satisfy both mechanical properties and estheticity, which is not possible for the conventional metal wire.

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

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

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

The in vitro cell functional tests on cell survival rate, LDH(Lactate Hydrogenase CII) protein released at the breakdown of cell membrane and superoxidized anion(O²⁻) using human neutrophils showed that Ni solution has the cell disruption effect. The deformed and disrupted morphology of neutrophils was confirmed by SEM observation. Whilst Ti and V solution showed the increase of superoxide anion and negligible change in the others, which suggests the cell stimulation effect. SEM observation confirmed that neutrophils are inflated with more complicated polyacicular morphology. One of the marking cytokines released at phagocytization, TNF- α , was not detected in any solution of Ni, V, Ti, the simulated body fluid(Hank's solution) mixed with 10 μ m particles of Ti and with submicron size Ni particles. TNF- α was found only in the 1-3 μ 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 μm and 10 μm Ti particles suggests that the particles(1-3 μm) smaller than cell size(about 5 μm in neutrophils) induces cytotoxicity as a result of phagocytosis, while for particles larger than cell size(10 μm) phagocytosis is not possible, resulting in the less clear cytotoxicity effect.

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

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

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

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

Laser lithography, one of the CAD/CAM systems to fabricate the polymer models by piling up the thin slices, which are photo-polymerized by scanning laser beam originally on the shallow depth of liquid epoxy monomer, was applied for the fabrication of dental prostheses of photo-curing composite resin composed of silica fillers in the matrix of high strength UDMA resin. The full dental crown could be fabricated using the shape data pre-designed by computer with high accuracy due to the smaller polymerization shrinkage than by

conventional methods. Then the functionally graded dental core and post with gradually changing filler content from 70 to 0% from the head of core abutment toward the apex of post was successfully fabricated. The stress concentration at the pulp root inserted with the conventional dental post has often caused the fracture in the surrounding dentin by impact force on the tooth crown. The stress relaxation effect by application of the functionally graded dental post was confirmed by simulation using the photoelastic method and finite element method(FEM).

(8) Radiation effects on polymer resin :

Radiation effects by C⁺ion, γ -ray from Co⁶⁰ and electrons on one of the main matrix polymer UDMA(urethane dimethacrylate) for dental composite resin were investigated with various mechanical tests and spectroscopies. C⁺ion radiation induced the large change in the structure sensitive properties of mechanical properties, Vickers hardness, flexural strength, abrasion resistance and little change in the non-structure sensitive properties of spectroscopies, FT-IR, Raman scattering, Fluorescence, NMR and thermal expansion coefficient. The results suggest that the mechanism of radiation effect is mostly due to the physical structure change such as lattice defects of vacancies, interstitials, depleted zone rather than the chemical effect of cross-linking by further progress of polymerization of residual monomers.

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

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

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

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

(11) Tissues and dental materials observation by XSAM

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

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

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

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

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

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

The current photocatalysis of anatase TiO₂ mostly works only by ultraviolet light. To make applicable for medical use it is necessary to develop the visible-light reactive photocatalysis. Visible light sensitization was obtained by

surface modification with cations of Au, Ag, Cu, Pt, Pd. Depigmentation with visible light around 470nm which is used for photopolymerization of composite resin restoration in dental clinics could be done with the Ag activated TiO₂ in contrast to very little effect in an untreated TiO₂. Antibacterial effect was also confirmed to streptococcus mutans, one of the most popular bacteria for caries. The application to bleaching of pigmented teeth was developed.

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

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

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

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

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

In order to identify and quantify the main influence parameters that determine the microparticle performance as drug delivery system, the mechanism of particle formation of biodegradable polyesters: poly(DL-lactide co glycolide)

and poly(L-Lactide), was investigated in their single and double emulsion formulation.

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

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

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

Other activities:

The three-year research project in nanomedicine under the subject of "Tissue Reaction and Biomedical Application of Nanotubes, Nanoparticles and Microparticles" has been continued for the second 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: Associate Prof.Mamoru OMORI (Institute for Materials Research, Tohoku University), Prof.Kazuyuki TOHJI(Department of Geoscience and Technology, Tohoku University), Prof.Toshiyuki HASHIDA(Fracture Research Institute, Graduate School of Engineering, Tohoku University), Prof.Yasunori TOTSUKA(Graduate School of

Dental Medicine, Hokkaido University), Prof.Takao KAWASAKI(Graduate School of Dental Medicine, Hokkaido University), Prof.Kohichi HANEDA(Department of Information Technology and Electronics, Ishinomaki Senshu University), Prof.Fumio NOGATA(Department of Human and Information Systems, Tohoku University) and other Collaborating Researchers. The fourth winter meeting was held at Noboribetsu Grand Hotel, Noboribetsu, Hokkaido on Feb.19-20. The fifth summer meeting was held at Hotel Sakan, Akyu, Miyagi on Sep.14-15. The annual report of the second year research project was published in March.

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

Dr.ROSCA Iosif Daniel of University Polytechnica Bucharest, Bucharest, Romania, finished the two years research activity on the development of polymer biomaterials of two year period as the invited researcher of the Japan Society for Promotion of Science (JSPS). The research collaboration is continuing between our laboratory and University Polytechnica Bucharest.

Prof.WATARI attended and made presentation in the Honorary Meeting for Profs.VAN LANDUYT and S.AMELINCKX of Belgian Society of Electron Microscopy, held at University of Antwerp(RUCA), Antwerp, Belgium on May 23.

Prof.WATARI and Mr.K.TAMURA attended the 16th Int.Symp.on Ceramics in Medicine at Porto, Portugal on Nov.6-9 and gave presentations.

The international collaborations are continued with Institute of Dental Materials Science, Umea University, SWEDEN (Emerita Prof. Maud BERGMAN) on application of Ti, ZrO₂, amalgam 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.

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

Diamond Cutter : Buehler and Struers diamond cutter

Presentations

Application of carbon nanotubes for dental materials and biomaterials, M.Uo, T.Akasaka, I.D.Rosca, F.Watari, K.Asakura, A.Yokoyama, M.Omori, Y.Sato, K.Tohji: The 26th Fullerene Nanotubes General Symposium, Okazaki, Jan., 2004.

Preparation of the carbon nanotubes mixed metal and resin for dental materials, M.Uo, T.Akasaka, I.D.Rosca, F.Watari, A.Yokoyama, M.Omori, Y.Sato, K.Tohji: 205th Symposium of Electro-Chemical Society, San Antonio, May, 2004.

The study of the fluorescent glass filler for composite resin, M.Uo, T.Akasaka, I.D.Rosca, S.Ohkawa, T.Sugawara, F.Watari, K.Tani, M.Morita: The 43th. General Session of the Japanese Society for Dental Materials and Devices. Tokyo, Apr., 2004.

XAFS analysis of surrounding tissue of the implant, M.Uo, T.Akasaka, F.Watari: The 44th. General Session of the Japanese Society for Dental Materials and Devices. Kyoto, Sept., 2004.

Carbohydrate Coating of Carbon Nanotubes for Biological Recognition; T. Akasaka, Y. Sato, K. Tohji, F. Watari : The 26th Fullerene-Nanotubes General Symposium, Okazaki, Jan., 2004.

Biomimetic Coating of Carbon Nanotube Surface; T. Akasaka, F. Watari, Y. Sato, K. Tohji : The 27th Fullerene-Nanotubes General Symposium, Yokohama, Jul., 2004.

Surface Modification of Carbon Nanotube by Biomimetic Coating; T. Aasaka, F. Watari, Y. Sato, K. Tohji : The 44th General Session of the Japanese Society for Dental Materials and Devices, Kyoto, Sep., 2004.

Carbohydrate Coating of Carbon Nanotubes for Biological Recognition; T. Akasaka, M. Uo, F. Watari, Y. Sato, K. Tohji : 206 th Meeting of The Electrochemical Society (ECS), Hawaii, Oct., 2004.

Surface Modification of Carbon Nanotubes by Adsorption of Artificial Glyco-Conjugate Polymers; T. Akasaka, F. Watari : 2004 Symposium of the Japanese Society for Biomaterials, Tsukuba, Nov., 2004.

Carbohydrate Coating of Carbon Nanotubes for Biological Recognition; T. Akasaka, M. Uo, F. Watari, Y. Sato, K. Tohji : International Symposium of Tissue Response and Biomedical Application of Carbon Nanotubes, Nanofibers, and Nanoparticles, Matsushima, Dec., 2004.

Elemental distribution of laser-weld zones of titanium and precious metals; K.Iwasaki, S.Ohkawa, M.Uo, T.Akasaka,T.Sugawara and F.Watari: The 44th. General Session of the Japanese Society for Dental Materials and Devices. Kyoto, Sep, 2004.

Cytokines emission of macrophages by carbon nano particle; K.Tamura, N. Takashi, M. Uo, Y. Totsuka, anf F. Watari: 26th Symposium of Fullerene-Nanotubes Research Association, Okazaki, Jan., 2004.

Size-Dependent Effects of micro/nano Dental Particles; K.Tamura, N. Takashi, M. Uo, Y. Totsuka, anf F. Watari: The 82st general Session of the International Association for Dental Research, Honolulu., Mar., 2004.

Effect of Nano-micro Particles on Organism; K.Tamura, N. Takashi, M. Uo, Y. Totsuka, anf F. Watari: The43rd general Session of Japanese Society For Dental Materials and Devices, Chiba, Apr 2004.

Biologic effects induced by micro/nano particles in vivo and in vitro study; K.Tamura, N. Takashi, M. Uo, Y. Totsuka, anf F. Watari: The 7th International Biomaterial, Sydney, May. 2004.

Biologic effects induced by Carbon nano particles; K.Tamura, N. Takashi, M. Uo, T. Akasaka, H. Kashiwazaki, K. Tohji, Y. Sato, Y. Totsuka, and F. Watari: 27th Symposium of Fullerene-Nanotubes Research Association, Tokyo, Japan, Jul., 2004.

Influence of particle and ion separated from Titanium Implant; K.Tamura, N. Takashi, M. Uo, T. Akasaka, H. Kashiwazaki, K. Tohji, Y. Sato, Y. Totsuka, and F. Watari: 46th Symposium of Japanese Association for Oral Biology, Hiroshima, Sep., 2004.

Effect of Nano-particles on Rat Macrophages in vivo and in vitro Study; K.Tamura, N. Takashi, M. Uo, T. Akasaka, H. Kashiwazaki, K. Tohji, Y. Sato, Y. Totsuka, and F. Watari: Symposium of Japanese Society of Biomaterial, Tsukuba, Nov, 2004.

Tissue Engineered bone construct: three-dimensional osteoblasts/mineralized collagen based composite: nHAC/PLA; Susan Liao, Fumio Watari, Fuzhai Cui: 16th Annual Meeting of Society for Artificial Organ and Regenerative Medicine, Sapporo, Jan., 2004

Evaluations of biocompatibility of nano-apatite/collagen biomimetic composite using neutrophils and osteoblasts; Susan Liao, Kazuchika Tamura, Fumio Watari: The 44th Japanese Society for Dental Materials and Devices, Kyoto, Sep., 2004

A novel method for carbonated hydroxyapatite/collagen composite; Susan Liao, Fumio Watari, Fuzhai Cui: Biomaterials in Regenerative Medicine: The Advent of Combination Products, Society for Biomaterials, Philadelphia, Pennsylvania, Oct., 2004.

The nano-hydroxyapatite/collagen based biomimetic materials for orthopaedics and dentistry; Susan Liao, Fumio Watari, Kazuchika Tamura, Shoji Ohkawa, Motohiro Uo: 2004 Symposium of the Japanese Society for Biomaterials, Tsukuba, Nov., 2004.

Diffusion of resin monomer to dentin and possibilities of strengthening, N.Kamishima, N.Ohata, M.Uo, S.Ohkawa, T.Akasaka, T.Sugawara, F.Watari: The 43th. General Session of the Japanese Society for Dental Materials and Devices. Tokyo, Apr., 2004.

LABORATORY OF ADVANCED MATERIALS CHEMISTRY

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The research activities of the laboratory are directed toward (1) formation, characterization and properties of nanocarbons, carbon-based composites and carbides, (2) anodizing of valve metal alloys for capacitor application as well as for improved wear resistance and (3) electrochemical and biological water treatments utilizing oxide and carbon materials.

Current research topics are in the following:

- (1) Formation and characterization of composite materials of carbon, ceramics and metals

Various carbon composites were formed by carbonization of 1) polyimide films containing metal complexes, 2) powder mixtures of organic polymer and ceramics and 3) chelate resins complexed with metal ions. Basic researches on the structure, composition, electric and magnetic properties of the composites are in progress by using XRD, TEM, SEM, Raman spectroscopy, SQUID, EIS and others.

- (2) Preparation of carbon nanofilaments using porous anodic alumina and etched aluminum foil templates

Porous anodic alumina and etched aluminum foils have been used as template materials to prepare carbon nanofilaments. Instead of usual CVD process we have prepared these nanocarbon materials simply by heating a mixture of the template and organic polymers, such as polyvinylalcohol and polyvinylchloride, which liquefy during carbonization process.

- (3) Anode characteristics of novel carbon nanofibers and Si-C-O glassy materials for lithium ion secondary batteries

Si-C-O glassy materials prepared from silicone and exfoliated graphite at elevated temperatures were examined to be used for anodes of lithium ion secondary batteries. The materials formed at selected conditions revealed very high charge-discharge capacity in addition to good cyclability. Further, anode characteristics of the carbon nanofilaments prepared by a template method were also examined.

- (4) Electrochemical wastewater treatment using oxide and carbon anodes

Various oxide anodes have been prepared by thermal decomposition of precursor salts on titanium substrate and anodic deposition. Using these anodes electrochemical decomposition of organic pollutants such as phenol, which are not easily decomposed by other methods, in wastewater has been examined to clarify the suitable electrochemical conditions and to develop effective anodes for their anodic decomposition. The electrochemical characteristics of various carbon anodes for wastewater treatment have been also examined.

- (5) Formation of barrier-type amorphous anodic films on titanium and niobium alloys

Alloying of titanium with other valve metals is found to result in the formation of uniform amorphous anodic films to relatively high voltages in neutral

and acid electrolytes, in contrast to an amorphous-to-crystalline transition of anodic films on titanium at low voltages. Such anodic films formed on the titanium alloys are possible candidates of new dielectric materials for electrolytic capacitors. The positive effects of several alloying elements on the dielectric properties and thermal stability of its anodic film on niobium for capacitor applications has been found recently.

(6) Plasma electrolytic oxidation of titanium alloys to improve wear resistance

Plasma electrolytic oxidation 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.

Other activities

Professor Konno attended International Conference on Carbon in 2004 (CARBON 2004) held at Brown University, Providence, USA in July and presented papers and served as a chairman. He also attended International Symposium on Nanocarbons 2004 (ISNC2004) held at Nagano in November.

Associate Professor Habazaki attended the 55th Annual Meeting of the International Society of Electrochemistry held at Thessaloniki, Greece in September and the 206th Meeting of the Electrochemical Society held at Honolulu, USA in October.

Facilities and Capabilities

Dc and rf magnetron sputtering : Shimadzu SP-2C, suitable for preparation of various metallic thin film materials as well as oxide and nitride films.

X-ray diffractometer: Rigaku RINT2000, capable of θ - 2θ and ω - 2θ modes measurements using Cu K α radiation.

Gas adsorption: Bel Japan Belsorp-Mini, capable of specific surface area / pore size distribution measurements at high precision.

Laser Raman Spectrometer: Jasco TRS-401 and Jobin Yvon T64000, triple type spectrometers with a Ar gas laser of 2W.

FT-IR spectrometer: Jasco FT-IR350, equipped with DR and RAS attachments.

Uv-vis spectrometer: Jasco V-550, equipped with DR attachment.

EPMA: JEOL JSM-5410 equipped with Oxford WDX-400.

TG/DTA: Seiko TG/DTA6300, temperature range room temp. to 1500°C.

TOC analyzer: Shimadzu TOC-5000A.

Capillary Electrophoresis analyzer: Ohtsuka Electronics CAPI-3100.

AFFILIATE MEMBERS

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Member of the committee of the Iron and Steel Institute of Japan for elucidation and control of corrosion protection of galvanized steels, of the committee for the study of *SABI* [rust] chemistry, and also of the organizing committee of the Ion Exchange Society. Research interests in the preparation and characterization of layered metal oxides and metal oxides in general as corrosion products from metals and as inorganic fine materials.

Presentations

Synthesis and Magnetoresistance Effect of $\text{Sr}_2\text{FeMoO}_6$ by the Molybdic Acid Gelation Method; M. Ito, T. Takeda, H. Tamura, and S. Kikkawa: The 42nd Symposium of Ceramics Science, Nagaoka, Jan., 2004.

Self-Organization of α -Fe Particles and Its Low Temperature Nitridation; K. Kubota, T. Takeda, H. Tamura, and S. Kikkawa: 2004 Annual Meeting of Ceramics Society, Fujisawa, Mar., 2004.

Intercalation of Vanadium Ions into Layered Manganese Oxide (Birnessite); H. Tamura, S. Kawanami, K. Nakamura, T. Takeda, and S. Kikkawa: The 84th Spring Meeting of the Japan Chemical Society, Nishinomiya, Mar., 2004.

Composition and Structure of Layered Manganese Dioxide Intercalated with Vanadium Ions; S. Kawanami, K. Nakamura, H. Tamura, T. Takeda, and S. Kikkawa: The 2004 Summer Joint Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Tomakomai, Jul., 2004.

Effect of the Kind of Raw α -Fe Powder Material on the Formation of Fe_{16}N_2 Magnet; K. Kubota, T. Takeda, H. Tamura, and S. Kikkawa: The 2004 Summer Joint Meeting

of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Tomakomai, Jul., 2004.

Preparation of Hydrotalcite-Magnetite Composite; J. Chiba, T. Takeda, H. Tamura, and S. Kikkawa: Ninth International Conference on Ferrites, San Francisco (USA), Aug., 2004.

Intercalation of Bio-Anions into Nano-Interlayers of Hydrotalcite; H. Tamura, J. Chiba, T. Takeda, and S. Kikkawa: The 57th Symposium of Colloid and Interface Chemistry, Onoda, Sept., 2004.

Stability of Corrosion Products from Galvanized Steels in the Presence of Atmospheric Carbon Dioxide, H. Tamura, The 148th Autumn Annual Meeting of the Iron and Steel Institute of Japan, Akita, Sept., 2004.

Synthesis of Vanadium-Ion Intercalated Manganese oxide (Birnessite) via Buserite; S. Kawanami, T. Takeda, H. Tamura, and S. Kikkawa: Joint Meeting of 206th Meeting of the Electrochemical Society and 2004 Fall Meeting of the Electrochemical Society of Japan, Honolulu (USA), Oct., 2004.

Preparation of Vanadium-Ion Intercalated Birnessite (Layered Manganese Oxide as Lithium-Ion Cathode); H. Tamura, S. Kawanami, K. Nakamura, T. Takeda, and S. Kikkawa: Joint Meeting of 206th Meeting of the Electrochemical Society and 2004 Fall Meeting of the Electrochemical Society of Japan, Honolulu (USA), Oct., 2004.

Synthesis and Magnetoresistance Effect of $\text{Sr}_2\text{FeMoO}_6$ by the Molybdic Acid Gelation method; M. Ito, T. Takeda, H. Tamura, and S. Kikkawa: 49th Symposium on Synthetic Crystals, Tsukuba, Nov., 2004.

Morphological Changes in the Hydrotalcite Crystals Deposited; J. Chiba, T. Takeda, H. Tamura, and S. Kikkawa: 49th Symposium on Synthetic Crystals, Tsukuba, Nov., 2004.

DISSIMILAR MATERIALS INTERFACE ENGINEERING LABORATORY

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The research activities of the laboratory are directed to an understanding of the mechanism of the high temperature corrosion in super alloys, inter-metallic compounds and iron-based alloys, and to the development of the corrosion resistant alloys and corrosion protection of materials with coating and surface modification. The research activity is also directed to an understanding of the solidification mechanism of metals and Alloys and to develop the modeling of casting structure using Phase-field, Cellular Automata, MonteCalro and Molecular Dynamics methods.

Current topics on research are in the following:

(1) High temperature sulfidation of alloys

Sulfidation properties of stainless steels, nickel alloys, and Ti-Al intermetallic compounds were investigated at relatively low sulfur pressures in H_2S-H_2 atmospheres.

(2) High temperature oxidation resistance of sulfidation processed Ti-Al alloys.

High temperature oxidation behavior of sulfidation processed Ti-Al intermetallic compound was investigated. Effect of the third element addition on the oxidation behavior was extensively investigated.

(3) High temperature corrosion under the atmosphere containing water vapor.

Oxidation behavior in Fe-Al and Fe-Si alloys under the atmosphere containing water vapor was studied. Acceleration of the oxidation was observed and its mechanism was investigated.

(4) Effect of Re coating on high temperature oxidation of super alloy.

Re was coated on the surface of a super alloy, and the oxidation behavior of the alloy was examined. A new method for coating Re on the surface of alloys based on electric plating was also investigated.

(5) Characterization of thermal barrier coatings

Thermal barrier coatings of the NiCrAlY-Zirconia composite were prepared by using Plasma Spray Coating Method and their mechanical and physical properties were investigated.

(6) Galvanizing process of steels by two step hot dipping

Galvanizing of steels was carried out by using a Zn-Al and a Zn-Al-Mg-Si molten alloys, and the optimum condition was investigated to make the galvanized layer having high corrosion resistance.

(7) Pb-free solder

Change in microstructure of a Pb-free solder due to composition and cooling rate during solidification was investigated. Effect of heat treatment on elastic modulus,

microstructure and hardness of the solder was studied.

(8) TLP Bonding

Dissolution and isothermal solidification behavior during transient liquid phase bonding process of Ni, Ni base alloys and Al were investigated based on both experiment and computer simulation.

(9) Prediction of solidification structure of casting

A method to simulate the macro structure of a casting was investigated by combining thermodynamics analysis, heat transfer calculation, Monte-Carlo Method and Cellular Automata Method.

(10) Simulation of microstructure development in solidifying alloy by Phase-field model.

The dendrite growth in the solidification process of an alloy was investigated by using a Phase-Field Model. Change in dendrite morphology due to thermal, solutal and fluid flow conditions was examined.

Other Activities

Prof. Narita Started the special research project ' Creation of diffusion barrier type bond coat to produce long life time, high reliable high temperature coating ' . The period of the project is 5 years and 10 researches participate in the project.

Assoc. Prof. K.Ohsasa attended the 4th International Conference on Physical and Numerical Simulation of Materials Processing held in Shanghai, China, May. Assoc. Prof. K.Ohsasa and Mr. Natsume attended the 6th Pacific Rim International Conference on Modeling of Casting and Solidification Processing, held in Kaohsiung, Taiwan, August. Assoc. Prof. K.Ohsasa and Mr. Natsume attended the 66th World Foundry Congress held in Istanbul, Turkey, September.

Presentations

Numerical Modeling of Solidification Structure Formation in Continuous

Casting process of Carbon Steel, M. Yamazaki, Y. Natsume and K. Ohsasa : North Forum of The Hokkaido Sec. of Iron and Steel Inst. Jpn., Muroran, March. 2004 .

Application of α -Cr Layer on the Ni-40Cr-W Alloys as the Diffusion Barrier Coating; Y. Taguwa, Y. Shibata, and T. Narita : The 134 th Annual Meeting of Jpn. Inst. Metals; Tokyo, Mar. 2004 .

Application of σ -Re-Cr-Ni Diffusion Barrier Coating on the Ni based Superalloy; D. Sumoyama and T. Narita : *ibid.*

Development of Oxidation Resistant Coating on Ni based Superalloy TMS-82+ ; H. Rang, K. Z. Thosin, and T. Narita : *ibid.*

Formation of Diffusion Barrier Coating on Hastelloy Alloy; K. Z. Thoshin, I. Sohn, H. Rang, Y. Katsumata, T. Narita, H. Yakuwa, and Y. Miyasaka : *ibid.*

Improvement of Spallation Resistance for Oxide Scale on Ni40Cr(X) Alloys; Y. Shibata, Y. Taguwa, T. Izumi, H. Takahashi, T. Takashima, M. Noguchi, and T. Narita : *ibid.*

Mechanical Properties of Surface Treated TiAl Alloys by Cr and Al Pack Cementation; T. Nishimoto, T. Izumi and T. Narita : *ibid.*

Phase-field Simulation for Solidification Structure Formation under Fluid Flow Condition, Y. Natsume, K. Ohsasa and T. Narita : The 147th Annual Meeting of Iron and Steel Inst. Jpn., Tokyo, March. 2004 .

Effects of Platinum on the Interdiffusion and Oxidation Behavior of Ni-Al-Based Alloys; B. Gleeson, W. Wang, S. Hayashi, and D. Sordelet: Proceedings of the 6th International Symposium on High Temperature Corrosion and Protection of Materials, Les Embiez, France, May, 2004 .

Prediction of Casting Structure Based On Heterogeneous Nucleation

Parameter, N.Nishiguchi and K.Ohsasa : Annual Meeting of 19 Committee of Jpn. Soc. Promotion of Science, Kobe, June 2004 .

Interdiffusion Behavior of Ni-based Superalloy/Re-Ni-Cr alloy/Ni; H. Matsumaru and T. Narita : Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, July.,2004 .

Formation of Re-Cr-Ni-W alloy as an Diffusion Barrier Coating on Nb-based Alloy; K. Saito, S. Hayashi and T. Narita : *ibid.*

Oxidation Behavior of Fe-Al Alloy; S. Mikuni, S. Hayashi and T. Narita : *ibid.*

Numerical Modeling of Solidification Structure Formation in Continuous Casting process of Carbon Steel, M.Yamazaki, Y.Natsume, K.Ohsasa and T.Narita : *ibid.*

Numerical Simulation of Dendrite Growth of Binary Alloys with Fluid Flow by Using Phase-field Method, Y. Natsume, K. Ohsasa and T. Narita : The 6th Pacific Rim International Conference on Modeling of Casting and Solidification Processing (MCSP2004), Kaohsiung, Taiwan. August 2004 .

Long-term Oxidation Behavior of Coated Ni based Superalloy TMS-82+ ; H. Rang, K. Z. Thosin, and T. Narita : The 135th Annual Meeting of Jpn. Inst. Metals; Akita, Sept. 2004 .

Formation of Diffusion Barrier Coating on Hastelloy Alloy; K. Z. Thoshin, H. Rang, T. Narita, and H. Yakuwa: *ibid.*

The Effects of Alloying Elements on Spallation Resistance of Oxide Scale on Ni₄O₂Cr Alloys; Y. Shibata, H. Takahashi, M. Noguchi, and T. Narita : *ibid.*

Development of Next Generation Bond Coating: T. Narita: *ibid.*

Interdiffusion Behavior of Ni-Al-Pt System; S. Hayashi, B. Gleeson, D. Sordelet, and T. Narita : *ibid.*

Improvement of Oxidation Resistance for γ -Cr Diffusion Barrier Coating with Zr addition; Y. Taguwa and T. Narita : *ibid.*

Long-Term Oxidation Behavior of Ni based Superalloy coated with various γ -Re-Cr-Ni Diffusion Barrier Coatings ; D. Sumoyama and T. Narita : *ibid.*

Formation and Assessment of Oxidation Resistant Coating on TiAl Alloy; T. Nishimoto, T. Izumi, and T. Narita: *ibid.*

The Mechanical Properties of TiAl Alloy Coated by a Two-step Cr and Al Diffusion Treatment; T. Nishimoto, T. Izumi and T. Narita: the 123rd committee on high temperature metals and alloys, Japan Soc. for Promotion of Science

Molecular Dynamics Simulation of Solidification of Iron, K. Ohsasa, Y. Natsume, H. Yasumoto and K. Matsuura : the 66th World Foundry Congress, Istanbul, Turkey, Sept. 2004 .

Numerical Simulation of Macrostructure Evolution in Al Base Multi-component Alloys Using a New Model coupled Cellular Automaton Method with Phase-field Method, Y. Natsume, K. Ohsasa and T. Narita : *ibid.*

Application of Reactive Casting to Coating and Joining of Aluminide Intermetallics, K. Matsuura, M. Kudoh, Y. Miyamoto and K. Ohsasa : *ibid.*

Multi-scale Modeling of Solidification Process -Nano-meso scale -, K.Ohsasa and Y.Natsume : The 14 8th ISIJ Meeting, International Organized Sessions, Akita, Sept.,2005.

Multi-scale Modeling of Solidification Process -Meso-macro scale -, Y. Natsume, K.Ohsasa : *ibid.*

Numerical Modeling of Solidification Structure Formation in Continuous

Casting process of Carbon Steel, M.Yamazaki, Y.Natsume, K.Ohsasa and T.Narita : The 14th Annual Meeting of Jpn. Foundry Engineering Soc., Kitakyusyu, Oct. 2004 .

Analysis of Negative Pressure in Solidifying Al-Si Alloy with Effect of Fluid Flow and Solid Deformation, K. Ohsasa and T. Ohmi : The 5th Pacific Rim International Conference on Advanced Materials and Processing, Beij ing, China, Nov., 2004

Corrosion Products on Zinc-coated Steels Detected by In-situ Raman Spectroscopy

Mikito Ueda, Masaru Matsuda and Toshiaki Ohtsuka
Galvatech '04 Conference Proceedings, 845

The corrosion products on zinc-coated steels were monitored by in-situ Raman spectroscopy.

- 1) When the amount of NaCl on surface is relatively large and the RH in the atmosphere is higher than 75%, aqueous ZnCl_2 layer was initially formed, following the formation of zinc hydroxy-chloride (ie., simonkollite), $\text{ZnCl}_2[\text{Zn}(\text{OH})_2]_4$. When the RH is lower, ZnO is only generated.
- 2) When the amount of NaCl is small, ZnO were only generated even at the RH higher than 75%, however, zinc hydrooxy-xhloride cannot be detected.
- 3) For the generation of zinc hydroxy-chloride, the formation of concentrated aqueous ZnCl_2 layer is an essential pre-step and the zinc hydroxy-chloride precipitated from the concentrated ZnCl_2 layer. The addition of Ni or Al into zinc coating, suppresses the generation of aqueous ZnCl_2 layer and zinc hydroxy-chloride.
- 4) The corrosion rate is order of pure zinc > Zn-12%Ni > Zn-5%Al.

Improvement of Resistance of TiAl Alloy against High Temperature Oxidation by Electroplating in AlCl_3 -NaCl-KCl- CrCl_2 Molten Salt

Mikito Ueda, Daigo Susukida, Shoichi Konda, Toshiaki Ohtsuka
Surface and Coatings Technology, 176, 202-208 (2004)

For improvement of the oxidation resistance of a TiAl alloy under high temperature conditions, aluminum chromium alloys were electroplated on the TiAl alloy in an AlCl_3 -NaCl-KCl molten salt containing CrCl_2 at 423 K. The deposit electroplated at -0.1 V vs. Al/Al^{3+} consists of $\gamma\text{-Al}_8\text{Cr}_5$ single phase, including chromium content at 41 at. %. A mixture phase of $\gamma\text{-Al}_8\text{Cr}_5$ and Al is, however, formed at potential from -0.2 to -0.4 V. The oxidation resistance of the electrodeposit layer was evaluated by a high temperature oxidation test at 1173 K for 24 h. On the TiAl specimen covered with $\gamma\text{-Al}_8\text{Cr}_5$ which was deposited at -0.1 V, a uniform AlCl_2 layer was formed during the oxidation at 1173 K. The AlCr_2 layer was covered by a thin dense Al_2O_3 . Both AlCr_2 and Al_2O_3 layers play a role of superior protection from the high temperature oxidation of the TiAl alloy; therefore, the plating of the $\gamma\text{-Al}_8\text{Cr}_5$ single layer deposited at -0.1 V reduced oxide thickness by 1/40 during the oxidation at 1173 K for 24 h from that on the TiAl without any plating.

Impedance Characteristics of Rust Layer and Its Interpretation

T. Ohtsuka

The 149th Symposium on Corrosion and Corrosion Protection – Symposium on Electrochemical Impedance Spectroscopy, JSCE (2004), p.81.

AC impedance was measured of the rust layer under wet condition. A simulation was made for the impedance with an equivalent circuit.

The impedance measured at frequencies between 10 and 100Hz is responsible to corrosion resistance of the rust layer. The issue of selection of equivalent circuits and the interpretation of the impedance response was discussed. (Japanese)

Rust Layers on Weathering Steels Exposed in Various Sites for 17 or 18 Years

T. Ohtsuka

The 145th Symposium of Corrosion and Corrosion Protection – SUBI [Rust] Chemistry for New Paradigm on Corrosion Engineering of Steel Bridges, JSCE (2004), p.73.

Characterization of the rust layers on weathering steels exposed in 7 sites in Japan for 17 or 18 years was made by 6 laboratories. The results were reviewed.

The weight loss of the weathering steel increases with air-borne salt. The rust layer formed in high concentration of air-borne salt includes β - and γ -FeOOH with relatively high concentration. The conductivity estimated by AC technique at about 100Hz under wet condition increases with the concentration of air-borne salt at the sites. The diffusion coefficient of water vapor in the rust and specific surface area of the rust measured by N_2 adsorption are also correlated with the concentration. (Japanese)

Consideration about the Definition of Molten Salt and Ionic Liquid

Koichi Ui, Mikito Ueda, Rika Hagiwara and Minoru Mizuhata
Molten Salt, 47, 114-123 (2004)

Is “the liquid composed entirely of ionic species exhibiting a melting point of around room temperature or lower” called room temperature molten salt or ionic liquid? The definition of these terms and differences are discussed. Currently defined ionic liquids are a part of molten salts or conventionally defined ionic liquids. They are composed of room temperature molten salts and salts of which the melting points do not significantly exceed 100°C. It is essential to recognize that there are two definitions for the term “ionic liquid”, current and original, which should be carefully distinguished in its use.

Maskless Dissolution Patterning of Al Film Using Localized Alkalization in the Vicinity of Small Electrode under Cathodic Polarization

Kazuhisa Azumi

J. Surf. Fin. Soc. Jpn. **55**, 929-932 (2004)

Dissolution patterning of thin sputter-deposited Al film formed on glass plate was examined by approaching a small electrode which was cathodically polarized. Hydrogen gas evolution on the small electrode causes alkalization of electrolyte solution around the electrode enough to dissolve Al film due to its amphoteric nature. Dissolution pattern less than 1 mm in size with dissolution width of ca. 0.1 mm was obtained using a thin Cu wire electrode approached to the Al film surface and scanned along the surface accompanying with cathodic polarization. (Japanese)

Potential Dependence of Normalized Friction Coefficient of Passive Iron Surface Evaluated by Nano-scratching in Solution

M. Chiba and M. Seo

Electrochim. Acta, **50**, 967-975 (2004)

Nano-scratching in solution was performed to the single-crystal iron (100) surface passivated at 0.0 V – 1.0 V (SHE) in pH 8.4 borate solution to evaluate the friction coefficient of the iron (100) surface kept in the passive state and its potential dependence. The friction coefficient obtained with nano-scratching for the passive iron surface depended on normal force, i.e., normal displacement, which resulted mainly from the geometry of the diamond tip. In order to avoid the effect of the tip geometry on friction coefficient, the normalized friction coefficient was newly defined with dividing friction coefficient by geometrical factor. The normalized friction coefficient obtained with nano-scratching in solution for the iron (100) surface kept in the passive state was significantly larger than those obtained with nano-scratching in air after passivation. The normalized friction coefficient obtained with nano-scratching in air after passivation was almost independent of potential in the passive region. On the other hand, the normalized friction coefficient obtained with nano-scratching in solution increased with increasing potential in the passive region.

The difference between normalized friction coefficients obtained with nano-scratching in solution and in air was discussed by taking into account a series of mechano-electrochemical reaction (film rupture, active dissolution and repassivation) which would take place at the moving front of the diamond tip during nano-scratching in solution. The large potential dependence of the normalized friction coefficient obtained with nano-scratching in solution were explained in terms of the increase in repassivation rate at the film rupture sites with increasing potential in the passive region. (English)

Changes in Surface Stress of Gold Electrode during Underpotential Deposition of Pb

M. Seo and M. Yamazaki

J. Electrochem. Soc., **151**(8), E276-E281 (2004)

The changes in surface stress of gold film electrode during underpotential deposition (UPD) of lead in pH 3.0, 0.5 M NaClO₄ solution containing 10⁻⁴ M Pb(ClO₄)₂ or PbCl₂ were measured by a bending beam method to investigate the relation between surface stress and structural change of Pb-UPD layer. A maximum in the surface stress versus potential curve like an electrocapillary curve emerged at onset of the UPD. Moreover, a hump in the surface stress versus potential curve also emerged in the range of surface coverage of Pb from $\theta_{pb} \approx 0.4$ to 0.8 during UPD process.

The changes in surface stress were plotted versus cathodic charge required for Pb-UPD. Two linear and one plateau regions appeared in the surface stress versus cathodic charge curve. The plateau region corresponded to the hump in the surface stress versus potential curve. It was deduced from the comparison with the STM, AFM and SXS results in literature that the plateau region is associated with the change in rotation angle from $R = 0^\circ$ to 2.5° of incommensurate hexagonal close-packed Pb layer. Particularly, it was emphasized that the hump resulted from the release of compressive surface stress due to the change in rotation angle of UPD layer. (English)

Determination of the Reduction Sequence in Cathodic Reduction of Duplex Copper Oxide Films Formed in Air

M. Watanabe, A. Sugimoto, M. Kodaira, M. Nakayama, M. Seo, Y. Ishikawa, A. Nishikata, T. Notoya, S. Furuya, R. Minamitani and Y. Miyata
Zairyo-to-Kankyo, **53**, 472-478 (2004)

The cathodic reduction of duplex air-formed oxide film on copper was performed at a constant current density of $i_c = -50 \mu\text{A cm}^{-2}$ in deaerated 0.1 M KCl solution to investigate the sequence of cathodic reduction of each oxide layer and its mechanism. The single-phase thick CuO film on copper was also cathodically reduced at $i_c = -50 \mu\text{A cm}^{-2}$ or -2.5mA cm^{-2} . The surface characterizations of the air-formed oxide film and single-phase CuO film before cathodic reduction and after partial or complete cathodic reduction were performed by XPS and X-ray diffraction, respectively.

The two plateau regions appeared in the potential vs. time curve during cathodic reduction of the duplex air-formed oxide film on copper, while one plateau region was observed in the potential-time curve during cathodic reduction of the single-phase CuO film on copper. The potential in the first plateau region for the air-formed film coincided with that in the plateau region for the CuO film. The results of XPS and X-ray diffraction suggested that in the first plateau region, the outer CuO layer is directly reduced to metallic Cu, while in the second plateau region, the inner Cu_2O layer is reduced to metallic Cu. (Japanese)

Analysis of Electroless Ni Plating on Al using Model Electrodes

K. Azumi, K. Nishimura, T. Kurihara and M. Seo
J. Surf. Fin. Soc. Jpn., **55**, 555-559 (2004)

In order to reproduce the initial process of the electroless plating of Ni on Al prepared with a double zincate pretreatment, a model electrode was prepared in which a small Zn tip was pressed to an Al plate. The immersion potential of the model electrode during plating was around -1 V for the first few seconds, which corresponds to the period of Zn dissolution, and then shifted to about -0.6 V which corresponds to electroless Ni plating on the Ni-P layer. By applying pressure to the Zn tip, it became possible to plate the Al specimen without zincate pretreatment. However, an anomalous deposition of Ni was sometimes observed around the Zn tip. This anomalous deposition was found to be formed at damaged areas such as the area to which the Zn tip was applied and the edges of the specimen. When these areas were coated, the time at which Ni deposition began was delayed and the distribution of Ni on the surface became uniform. Based on these results, the function of zincate pretreatment in electroless Ni plating was considered. (Japanese)

Performance of Microelectrode Vibrating above an Insulator Surface

K. Fushimi, K. Azumi, M. Seo
Electrochemistry Communications, **6** (2004) 959-963

Voltammetry of a microelectrode that vibrated ultrasonically in a lateral direction showed some unique electrochemical phenomena coupled with hydrodynamics. Vibration of the microelectrode increased the current flowing through the microelectrode at definite frequencies. At the definite frequencies, the approach of the vibrating microelectrode to an insulator surface also increased the current with decreasing distance in the vicinity of the insulator, phenomena that were ascribed to deformation of the diffusion layer on the electrode due to motion of the solution.

Cathodic Dissolution Behavior of Aluminum Wire Electrode in Solutions Containing Borate and Sulfate Ions

K. Azumi, T. Ueno and M. Seo
J. Electroanal. Chem., **567** (2004) 1-7

Dissolution of Al wire electrodes due to local alkalization induced by the hydrogen evolution reaction under conditions of cathodic polarization in neutral solutions containing K_2SO_4 and borate ions was examined using resistometry. The dissolution rate increased almost linearly with increase in the cathodic current, and about 30-40% of OH^- ions generated by the hydrogen evolution reaction was used to form $Al(OH)_4^-$ ions. The dissolution depth calculated from the resistance change increased linearly with the increase in concentration of SO_4^{2-} ions. In K_2SO_4 solutions, Al dissolved uniformly and provided a porous surface. In a mixture of K_2SO_4 solution and borate solution, however, non-uniform dissolution occurred due to formation of large pits. Such non-uniform dissolution is due to the buffer capacity of borate ions in the weakly alkaline range.

Mechanical Properties of the Single-Crystal Iron Surfaces Kept at Passive State in Solution

M. Seo and M. Chiba

Proc. 8th. Ultra-Steel Workshop, NIMS, Tsukuba, p. 90-95 (2004)

Nano-indentation and nano-scratching in solution were made on the single-crystal iron (100) or (110) surface controlled electrochemically at passive state in aqueous solution from the viewpoint of nano-mechano-electrochemistry. Moreover, the cyclic nano-indentation in solution was performed on the passive iron surfaces after and without dichromate treatment to evaluate the roles of dichromate treatment in improvement of corrosion resistance.

The hardness obtained with nano-indentation in solution for the passive iron (110) surface kept at a constant potential in pH 8.4 borate solution was larger than that for the passive iron (100) surface. The potential dependence of hardness for the passive iron (110) and (100) surfaces indicated that the hardness of the passive surface is the composite hardness of the passive film and the substrate iron. The hardness of the passive film itself was larger than that of the substrate iron.

The dichromate treatment increased the hardness of the passive iron surface. The effect of dichromate treatment on hardness was significant in solution, which was explained in terms of the promotion of repassivation at the ruptured sites due to chromium-enriched film in solution. The cyclic nano-indentation in solution supported the above explanation.

The friction coefficient obtained with nano-scratching in solution for the passive iron (100) surface kept at a constant potential in pH 8.4 borate solution was always larger than that obtained with nano-scratching in air after passivation. The friction coefficient obtained with nano-scratching in solution increased with increasing potential, while that obtained with nano-scratching in air had no significant potential dependence. The significant potential dependence of friction coefficient obtained with nano-scratching in solution was explained in terms of the potential dependence of repassivation rate at the ruptured sites of passive film.

Recent Progress and Future Prospect in Corrosion Science - Approaches by Using New Techniques-

Masahiro Seo

Zairyo-to-Kankyo, **53**, 162-166 (2004)

New novel techniques for surface characterization on an atomic level have been developed rapidly during past two decades. These techniques have been applied to corrosion research and provided great advances in corrosion science. In this article, their application results in corrosion science were reviewed focusing on scanning probe microscopic techniques such as Kelvin microprobe, scanning electrochemical microscopy, and scanning tunnel microscopy. Moreover, it was emphasized that quartz crystal microbalance gave the great contribution to study on minute corrosion of metal thin films. (Japanese)

Initial Stage of Localized Corrosion on Zn-5mass% Al Coated Steels with Photon Rupture Method in Cl⁻ Solutions

Masatoshi SAKAIRI, Kazuma ITABASHI and Hideaki TAKAHASHI

Proc. of Galvatec '04, 1035-1043, (2004)

Zinc and zinc alloy coated steels are widely used, because of their high performance of corrosion resistance. In the present study, protective nitrocellulose film which was formed on specimens was removed by photon rupture method at constant potentials in 0.5 kmol m⁻³ H₃BO₃ - 0.05 kmol m⁻³ Na₂B₄O₇ (pH = 7.4) with chloride ions to investigate the effect of potential and chloride ions at the initial stage of localized corrosion of Zn - 5mass% Al coated layer. The nitrocellulose film on the specimen can be removed locally by the photon rupture method. In solutions with 0.1 kmol/m³ NaCl, oxide films are reformed at low E_a after removal of the nitrocellulose film. At high E_a, localized corrosion occurs with forming corrosion products in chloride ion containing solutions at the nitrocellulose film removed area. (English)

Localized Removal of Aluminum Hard Anodic Oxide Film by Pulsed YAG Laser Irradiation

Sakairi Masatoshi, Yamashita Shingo, Takahashi Hideaki, Shimamura Kiyotaka,
Katayama Naoki and Abe Yoshihiko

J. Surf. Fin. Soc. Jpn., **55**, 349-354 (2004)

A laser beam micro surface finishing method attempted to remove hard anodic oxide film formed on aluminum specimens. The hardness of the film increases with increasing applied current density during anodizing and decreasing concentration of SO_4^{2-} ions. Specimens were irradiated in solutions with a pulsed Nd-YAG laser beam through a convex lens with 60 mm focal length to remove anodic oxide film locally. Thin anodic oxide film can be removed without cracks by one pulse of laser irradiation, but thick oxide films need several pulses of irradiation removed without cracks. Thick as grown hard anodic oxide film was removed leaving numerous cracks and the size of the removed area increased with irradiation time. However, dyed thick anodic oxide film was removed layer-wise at low irradiation power without cracks, because the dyed oxide film absorbed laser energy. The size of removed area of the dyed film did not change with irradiation time. (Japanese)

Fabrication of Three-dimensional Microstructures by Aluminum Anodizing, Laser Irradiation, and Metal Deposition

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

Proc. ASST 2003, 117-122 (2004)

Three-dimensional microstructures, electrochemical micro-reactors, plastic-injection molds, cylindrical network structures were fabricated by four sequential processes: porous anodic oxide film formation, pore sealing, laser irradiation, electroplating or electroless-plating.

In the fabrication of the plastic injection mold, aluminum blocks carved by electric discharge machining were covered with hard anodic oxide films, and then irradiated with a pulsed Nd-YAG laser at the carved area to remove the anodic oxide film locally. Finally, relatively thick Ni-P alloy layers were deposited on the film-removed surface by electroless-plating.

In the fabrication of the electrochemical micro-reactor, through-holes, grooves, and a square chamber were carved by laser irradiation on the surface of aluminum plates after anodizing, and then a gold thin layer was deposited on the surface of the chamber. The electrochemical cell with a volume of 1 μ l showed good performance in the measurements of cyclic voltammograms.

Cylindrical network structures were fabricated, using cylindrical aluminum pipes. The aluminum pipe was covered with porous anodic oxide films, and then irradiated with a pulsed Nd-YAG laser in a Ni plating solution to remove the oxide film locally by rotating and moving up / down with an XYZ stage. Nickel was electroplated at the film-removed area before removing the aluminum substrate and anodic oxide films in NaOH solutions. (English)

Behavior of Second-Phase Particles in Al5052 Alloy during Anodizing in a Sulfuric Acid Solution -Confocal Scanning Laser Microscopic Observation-

S.-M. Moon, M. Sakairi, and H. Takahashi

J. Electrochem. Soc., **151**, B399-B405 (2004)

The behavior of second-phase particles during anodizing of Al5052 alloy in 16 wt % sulfuric acid solution was investigated by confocal scanning laser microscopy (CSLM). Two different types of second-phase particles were observed in the Al5052 alloy: Al-Mg particles and Al-Mg-Fe particles. The Al-Mg particles showed a groove type morphology because of selective dissolution of Mg during anodizing, while Al-Mg-Fe particles showed a protrusion type morphology in the CSLM height image (top view). The CSLM contrast image of cross-sections of the anodic oxide film showed the presence of two different types of imperfections in the anodic oxide film: bright and dark type imperfections. The bright type imperfections were determined to contain metallic iron, indicating that the metallic iron had been transferred from the substrate into the oxide film without oxidation during anodizing, this reflects the incident laser beam strongly to give a bright CSLM contrast image. The dark type imperfections were explained by a scattering of the laser beam with vacant or irregular-structured regions, resulting from the selective dissolution of Mg. (English)

Change in the Structure and Dielectric Properties of Niobium Anodic Oxide Films during Potentiostatic Anodizing

K. Nagahra, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, and Y. Oda

Electrochemistry, **72**, 624-632 (2004)

Niobium specimens with chemical polishing were anodized in a phosphoric acid solution galvanostatically up to $E_a = 100$ V, and then potentiostatically at $E_a = 100$ V. During galvanostatic anodizing, anode potential increased almost linearly with time, while, during potentiostatic anodizing, anodic current decreased with time before $t_{pa} = 3.6$ ks, and then increased slowly before decreasing again at $t_{pa} = 32.4$ ks. Galvanostatic anodizing allowed compact oxide films to grow at a steady rate, and also micro imperfections to form in the film at the ridge of convex network structure produced by chemical polishing. The imperfections grew during potentiostatic anodizing, showing the cracking and rolling-up of the oxide film as well as the formation of crystalline oxide at the center of the imperfections. Long-term anodizing lead to the coalescence of the imperfections and eventually the covering of all surfaces with imperfections. Parallel equivalent capacitance, C_p , of anodic oxide films decreased with t_{pa} before 3.6 ks, and increased after 3.6 ks, while the dielectric dissipation factor, $\tan \delta$, remained to a small value before 3.6 ks, and increased with t_{pa} after 3.6 ks. Measurements with higher bias voltages caused less dielectric dispersion of anodic oxide films. The mechanism of structural change of anodic oxide films during potentiostatic anodizing, and the correlation between the structure and dielectric properties of anodic oxide films are discussed. (Japanese)

Influence of Current Density on the Structure and Dielectric Properties of Anodic Oxide Films on Niobium

K. Nagahra, M. Sakairi, H. Takahashi, S. Nagata, K. Matsumoto, K. Takayama, and Y. Oda

J. Surf. Fin. Soc. Jpn., **55**, 943 – 951 (2004)

Niobium specimens with chemical polishing were anodized in a phosphoric acid solution galvanostatically at $i_{a,ini} = 1, 10, 100$ and 1000 Am^{-2} up to $E_a = 100 \text{ V}$, and then potentiostatically at $E_a = 100 \text{ V}$ for $t_{pa} = 7.2 \text{ ks}$. During galvanostatic anodizing, anode potential increased almost linearly with time on all the specimens, while, during potentiostatic anodizing, anodic current decreased with time. The current density at $t_{pa} = 7.2 \text{ ks}$ was higher at lower $i_{a,ini}$ in the range of 0.02 to 0.25 Am^{-2} . The spectra of Rutherford backscattering spectroscopy (RBS) and glow discharge optical emission spectroscopy (GD-OES) showed that higher $i_{a,ini}$ causes film thickness to decrease and the amount of incorporated phosphorus to increase. Micro imperfections were formed in the film at the ridge of convex network structure produced by chemical polishing, and the number of imperfections decreased with increasing $i_{a,ini}$. Parallel equivalent capacitance, C_p , and the dielectric dissipation factor, $\tan \delta$, of anodic oxide films decreased with increasing $i_{a,ini}$. The mechanism of decrease in the number of imperfections in anodic oxide with increasing $i_{a,ini}$ is discussed in term of film thickness, phosphorus incorporation and Nb^{5+} transport number. (Japanese)

Structures, Morphology, Dielectric Properties of Nanocomposite Oxide Films Formed by Anodizing of Sputter-Deposited Ta-Al Bi-layers

A. Mozaley, M. Sakairi, and H. Takahashi

J. Electrochem. Soc., **151**, F257-F268 (2004)

Anodizing of Ta-Al bilayers (aluminum deposited on tantalum) was performed in 0.2 M $\text{H}_2\text{C}_2\text{O}_4$ solution to transform the aluminum metal into its nanoporous oxide followed by pore widening and reanodizing to different voltage in the range of 100-600 V. The anodic films consist of an upper layer of nano-sized tantalum columns penetrating into the pores and a lower layer of continuous tantalum oxide under the porous alumina film. The columns are mainly composed of tantalum pentoxide and tantalum sub-oxides TaO_2 , Ta_2O_3 , and TaO while the lower film layer is tantalum monoxide. At the boundary between the columns and alumina cells, a region of mixed (composite) Ta_2O_5 and Al_2O_3 is formed due to channeling of the ionic current through the outer part of the alumina cell walls. The relationship between the layers and the ionic transport during oxide growth depend on pore size and formation voltage. The dielectric properties of the anodic films are close to those of an ideal capacitor. Voltage-independent apparent dielectric constant of 12.6 was determined for the films formed by normal reanodizing. The relatively higher dielectric constant for the films formed by reanodizing through the widened pores risen from 17.6 to 24.0 in the voltage range of 270-400 V, which is due to the change in morphology, relative amount and chemical composition of anodic tantalum in the complex film structure. The nanocomposite anodic films can be used as dielectrics for high-voltage low-leakage current electrolytic capacitors. (Japanese)

Formation of Al / Nb Composite Oxide Films by Sol-Gel Coating / Anodizing

K. Watanabe, M. Sakairi, H. Takahashi, S. Nagata, and S. Hirai

J. Surf. Fin. Soc. Jpn., **55**, 471 – 477 (2004)

Aluminum specimens coated with niobium oxide by a sol-gel method were galvanostatically anodized in a neutral borate solution. The time-variations in anode potential during anodizing was monitored, and the structure and dielectric properties of the anodic oxide film were studied by TEM, EDX, RBS, and electrochemical impedance measurements.

It was found that the anode potential increases linearly with time after a rapid increase in potential at the initial period of anodizing. During anodizing, an anodic oxide film, which consisted of an inner Al_2O_3 layer and an outer Al-Nb composite oxide layer, grew at the interface between Nb_2O_5 layer and the aluminum substrate. The interface between the outer and inner layer became vaguer as potential rises and the concentrations of aluminum and niobium ions in the composite oxide layer also changed. The capacitance of the specimen after sol-gel coating and anodizing was 150% as large as that without sol-gel coating. This is due to a high dielectric constant of the composite oxide layer.

The mechanism of anodic oxide films growth on the specimen coated with Nb_2O_5 is discussed in terms of the pore distribution in the Nb_2O_5 layer and the transport of Nb-cations across the anodic oxide film during anodizing (Japanese).

Rapid Analysis of Metallic Dental Restorations using X-ray Scanning Analytical Microscopy

M.Uo and F.Watari

Dental Materials, 20, 611-615 (2004)

X-ray scanning analytical microscopy (XSAM) makes it possible to analyze small specimens in air without pretreatment. The purpose of this study was to utilize XSAM for the rapid analysis of metallic dental restorations by microsampling. Six different dental alloys were scratched with brand-new silicone points to obtain metal on the silicone point for compositional analysis. The fluorescent spectra of XSAM were measured to determine the metal attached to the specimen. The major components of the six dental metals, except for palladium, were clearly detected. The identification of palladium was difficult since the fluorescent X-ray of palladium is quite close to that of rhodium, which is the source metal of the incident X-rays. However, with a slight modification of XSAM, palladium was also identified. The total time required for sampling and analysis with XSAM was less than 10 min. The amount of the attached metal was estimated to be less than 30 mg. This amount of sampling does not damage metal restorations. XSAM analysis using the microsampling technique is useful for the rapid analysis of metallic restorations.

Quantitative Analysis of Biologic Specimens by X-Ray Scanning Analytic Microscopy

M.UO, M.Tanaka and F.Watari

J.Biomed Mater Res Part B: Appl Biomater 70B: 146-151 (2004)

X-ray scanning analytic microscopy (XSAM) can be used to visualize the elemental distribution in biologic specimens. In this article, the authors prepared standard specimens for XSAM and performed quantitative analysis of various elements dissolved in soft tissues. Two different types of standard specimens were prepared. Methylmethacrylate (MMA) resin-based standard specimens were prepared with organic compounds of elements for low-concentration standards and lithium borate glass-based standard specimens were prepared with oxides of elements for higher concentration standards. Using these standard specimens, the P and Ca concentrations in normal rat tissue and dissolved Ni, Fe, and Ni concentrations around metalimplanted tissues were quantitatively analyzed. The estimated concentrations of dissolved Fe, Cu, and Ni from the implants were 1000, 40, and 20 mM, respectively. From the concentration levels causing inflammation around these implants, the high toxicity for soft tissue of Ni and Cu at low concentrations, for example, 10 mM, was confirmed. The toxicity of Cu was estimated as next to that of Ni. In contrast, Fe had low toxicity despite high concentrations of dissolved Fe of as much as 1000 mM. In this article, it was possible to estimate the nonmetallic elements and lowconcentration metallic elements dispersed in soft tissue by XSAM.

Laser Welding of Titanium and Dental Precious Alloys

K.Iwasaki, S.Ohkawa, M.Uo, T.Akasaka and F.Watari

Materials Transactions, 45, 1140 - 1146 (2004)

The performance of laser welding of Ti and two dental precious alloys (Ag-Pd-Au, Au-Pt-Ag) was investigated by mechanical testing and microscopic observation, using butt joint as design. The laser irradiation was done using a commercial Nd:YAG dental laser-welding device in a single pulse mode with output currents 150, 200, 250, 300 A, spot diameters 0.6, 0.9, 1.2 mm, and pulse duration 10 ms. The average welding fracture strength of the dissimilar metals were 108.9 and 137.2 MPa for Ti and Ag-Pd-Au alloy, and Au-Pt-Ag alloy, respectively. The average welding fracture strength of the same metals were 594.9, 648.8 and 312.9 MPa for Ti, Ag-Pd-Au alloy and Au-Pt-Ag alloy. The hardness increased in weld zone, compared with the base metals. Penetration depths were affected by the welding conditions such as the output currents and spot diameters. The welding cracks and porosity were observed in microstructures of the welds. Mapping by EPMA showed the remarkable heterogeneity of the component metals concerned. The welding cracks, porosities and granular precipitates similar to metallic compounds in the weld zones were suggested as the cause for lower welding fracture strength in the dissimilar welds, compared with the similar metals.

Distortion of Laser Welded Titanium Plates

K. Iwasaki, S. Ohkawa, Iosif D. Rosca, M. Uo, T. Akasaka and F. Watari

Dental Materials Journal, 23, 593 - 599 (2004)

The distortion of laser welded titanium plates was assessed for different operating conditions of the laser welding device, and different welding parameters: weld point, and prewelding. In this study Nd:YAG laser welding device was used for joining the titanium plates. The results showed that the distortion increased stepwise after each welding point along the welding (one-side welding), and decreased consecutively as the welding proceeded on the second side of the welding (two-side welding). High current and large spot diameter produced increased distortion in the case of one-side welding, but increased recovery for the two-side weld. The current and the spot diameter determine the weld pool which in turn regulates the distortion based on shrinkage. Four-point prewelding decreased significantly the final distortion both for one and two-side welds. Alternating two-side welding of the prewelded assembly showed similar distortion as the classic two-side weld.

Three-Dimensional Topographic Scanning Electron Microscope and Raman Spectroscopic Analyses of the Irradiation Effect on Teeth by Nd:YAG, Er:YAG, and CO₂ Lasers

M.K.Yamada, M.Uo, S.Ohkawa, T.Akasaka and F.Watari

J Biomed Mater Res Part B: Appl Biomater 71B: 7-15 (2004)

A three-dimensional analyzer installed in a scanning electron microscope was used to evaluate the morphology and surface roughness using noncontact profilometry. Observations were carried out on the enamel and dentin surface irradiated by three different lasers: Nd:YAG (wavelength 1.06 μm), Er:YAG (2.94 μm), and CO₂ (10.6 μm). Spectroscopic analysis was done by Raman spectroscopy for nonirradiated and laser-irradiated surfaces. The lasers were applied perpendicularly to vertically sectioned and polished human extracted caries-free molars. The tooth was sectioned at each cavity for cross-section analysis after laser irradiation. Irradiation by Nd:YAG and CO₂ lasers of the enamel surface showed an opaque white color, different from dentin where the surface turned black. The Er:YAG laser induced no changes in color of the dentin. Numerous cracks associated with thermal stress were observed in the CO₂ laser-irradiated dentin. Noncontact surface profile analysis of Er:YAG laser-irradiated enamel and dentin showed the deepest cavities, and direct cross-sectional observations of them showed similar cavity outlines. The CO₂ laser-irradiated dentin had the least surface roughness. Raman spectroscopic analysis showed that fluorescence from the laser-irradiated tooth was generally greater than from nonirradiated teeth. Bands in dentin attributed to organic collagen matrix were lost after Nd:YAG and CO₂ laser irradiation, and a broad peak due to amorphous carbon appeared. The Er:YAG laser-irradiated dentin showed no sign of a carbon band and had more suitable results for dental ablation. Noncontact surface profile analysis was effective to evaluate the structural change in the tooth in the microarea of study after laser irradiation.

Anodic Oxidation of Mg-Cu and Mg-Zn Alloys

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

Electrochimica Acta, **49**, 899-904 (2004)

Metastable, solid-solution. Mg-0.8 at.% Cu and Mg-1.4 at.% Zn alloys have been anodized up to 250 V at 10 mA cm⁻² in an alkaline phosphate electrolyte at 293 K in order to investigate the enriching of alloying elements beneath the anodic films. Rutherford backscattering spectroscopy (RBS) revealed enrichments to about 4.1 x 10¹⁵ Cu atoms cm⁻² and 5.2 x 10¹⁵ Zn atoms cm⁻², which correlate with the higher std. Gibbs free energies per equiv for formation of copper and zinc oxides relative to that for formation of MgO. The enriched layers were of thickness about 1.5-4.0 nm by medium energy ion scattering (MEIS). The anodic films, composed mainly of magnesium hydroxide, contained copper and zinc species throughout their thicknesses; the Cu:Mg and Zn:Mg at. ratios were about 18 and 25% of those of the alloys, respectively. Phosphorus species were present in most of the film regions, with a P:Mg at. ratio of about 0.16. The magnesium ions in the film account for about 30% of the charge passed during anodizing.

Effect of Copper Enrichment on the Electrochemical Potential of Binary Al-Cu Alloys

S. Garcia-Vergara, F. Colin, P. Skeldon, G. E. Thompson, P. Bailey, T. C. Q. Noakes, H. Habazaki and K. Shimizu

Journal of the Electrochemical Society, **151**, B16-B21 (2004)

Using Al-Cu alloys, containing between 0.1 and 26 atom % Cu, deposited by magnetron sputtering and etching in sodium hydroxide solution, enrichments of copper have been developed selectively in the alloys. Rutherford backscattering spectroscopy and medium energy ion scattering quantified the enrichments and their locations just beneath the alumina-based oxides remaining from the etching. In some cases, the enrichment was sufficient for oxidation of copper to take place; in other cases, it was not, so that only aluminum was oxidized, with copper being confined to the alloy, enriching in an alloy layer about 2 nm thick. The potentials of the etched alloys in 0.1 M ammonium pentaborate solution at 293 K increased as the copper content of the enriched alloy layer increased. The enrichment of copper in the alloy beneath an alumina-based film free of copper species, i.e., without requirement for oxidation of copper and incorporation of copper species into the oxide, was sufficient to generate increases in potential of similar magnitude to those found for specimens in which oxidation of copper had taken place. The potential increased by approximately 410 mV with an increase in the level of enrichment to approximately 6.5×10^{15} Cu atoms cm^{-2} .

Formation of Iron Dispersed Graphite Composites Utilizing Exfoliated Graphite and Their Magnetic Properties

H. Konno, Y. Takahashi and H. Habazaki

Tanso, **214**, 191-193 (2004)

An organic solution of tris(acetylacetonato) iron(III) was impregnated by sorption into exfoliated graphite and dried at 180°C in air. By 1 h treatment of this precursor at 900-1200 °C in Ar (heating rate to each temp.: 400 K h⁻¹), Fe/graphite composites containing 33% Fe were obtained. In these composites fine a-Fe particles of several tens to hundreds nm were uniformly dispersed, though the surface of some particles may be oxidized by exposure to air. For the 1000 °C product, magnetization assigned for Fe was 154 emu g⁻¹, and the coercive force, H_c, 420 Oe.

Chromate Conversion Coatings on Aluminium-Copper Alloys

Y. Liu, P. Skeldon, G. E. Thompson, H. Habazaki and K. Shimizu

Corrosion Science, **47**, 341-354 (2004)

The study compares the formation of chromate/fluoride conversion coatings, composed mainly of amorphous hydrated chromia, on model, solid-solution, binary Al-Cu alloys, of a range of compositions, and on 2014-T6 aluminum alloy. The model alloys, produced by magnetron sputtering, reveal the importance of copper in limiting the thickness of the coatings by promoting loss of coating material. This occurs at an earlier time in the treatment with increasing copper content of the alloy. The coating loss follows closely upon the achievement of the required level of copper enrichment for incorporation of copper into the coating, with a thin alumina film beneath the hydrated chromia sustaining the enrichment process. The coating on the 2014-T6 alloy is of non-uniform thickness, with much thinner coating developing at copper-rich second phases, consistent with the results of model alloys.

Composition and Density of Non-Thickness-Limited Anodic Films on Aluminium and Tantalum

Q. Lu, P. Skeldon, G. E. Thompson, H. Habazaki and K. Shimizu

Thin Solid Films, **471**, 118-122 (2004)

The unusual occurrence of anodic films of unlimited thickness was recently reported for anodizing of Ta in certain dehydrated, high-temp. electrolytes with org. solvents. The precise nature of these films is still uncertain. Non-thickness-limited (NLT) anodic films were formed at 0.1 mA cm^{-2} on Al and Ta in glycerol/phosphate electrolyte at 453 K and then examined by Rutherford backscattering spectroscopy (RBS). The results disclosed films composed of alumina and tantalum, free of P species at the resolution of the measurements. Most notably, the densities of the NLT alumina and tantalum were approx. 2.4 and 3.6 g cm^{-3} , respectively. These values are less than those of compact anodic films usually grown at high efficiency in aqueous electrolytes by respective factors of approximately 1.3 and 2.2. This difference in d. is attributed primarily to the morphology and structure of NLT film materials, which incorporate significant porosity.

Ageing Effects in the Growth of Chromate Conversion Coatings on Aluminium

Y. Liu, A. M. Arenas, S. G. Garcia-Vergara, P. Skeldon, G. E. Thompson, K. Shimizu and H. Habazaki

Corrosion Science, **47**, 145-150 (2004)

Conversion coatings have been formed in two stages on sputtering-deposited aluminum using a chromate/fluoride bath. The first stage, common to all specimens, was conversion treatment for 1 min to produce a coating of thickness of about 70 nm, with associated thinning of the aluminum substrate. Further treatment was then carried out for 13 min, either immediately or with intervening ageing in humid air, water or laboratory air. Notably, ageing in laboratory air for 1 h was sufficient to prevent significant growth of new coating material upon re-immersion in the coating bath. In contrast, ageing in humid air or water allowed additional thickening of the coating, although with a reduced growth rate. The behavior appears to be related to loss of free or weakly bound water from the coatings in laboratory air, with the composition and structure of the coating being modified such that transport of reactant and product species of the coating process is impeded.

Transport Numbers of Metal and Oxygen Species in Anodic Tantalum

Q. Lu, P. Skeldon, G. E. Thompson, D. Masheder, H. Habazaki and K. Shimizu

Corrosion Science, **46**, 2817-2824 (2004)

The transport numbers of metal and oxygen species have been determined in amorphous anodic tantalum films, using transmission electron microscopy to locate ion-implanted xenon marker layers within the films. The films were formed on sputtering-deposited tantalum at constant current density, in the range 0.01-10 mA cm⁻², in 0.06 wt% H₃PO₄ solution at either 20 or 85 °C. The films grow by migration of metal and oxygen species through the film thickness, with formation of new film material at the film/electrolyte and metal/film interfaces respectively. The cation transport number, t^+ , increases due to either increase in current density or decrease in temperature: for current densities in the selected range, t^+ increases from 0.18 to 0.32 at 20 °C, and from 0.14 to 0.29 at 85 °C. Low concentrations of phosphorus species, incorporated into an outer layer of the film, migrate inward during film growth. The migration rates are slower than those of oxygen species, by a factor in the range 0.2-0.3.

Examination of Surface Films on Aluminum and Its Alloys by Low-Voltage Scanning and Scanning Transmission Electron Microscopy

K. Shimizu, H. Fujitani, H. Habazaki, P. Skeldon and G. E. Thompson

Corrosion Science, **46**, 2549-2561 (2004)

The potential of low-voltage, high-resolution scanning and scanning transmission electron microscopy (SEM/STEM) for morphological characterization of various surface insulating films on aluminum and its alloys was assessed by examination of porous anodic films, barrier anodic films and corrosion product layers. The characterization shows clearly the value of the approaches, particularly the ability to image directly fine details of appropriately-prepared aluminum surfaces that have usually required examination by TEM. Such ready characterization assists mechanistic understanding of the contributions of the macroscopic surface and flaws or second phase to the filming and corrosion processes. Further, the approaches are applicable to other materials where such understanding was limited by the sample preparation routes available for TEM.

Reducing Gas Sensing Based on the Redox Interconversion of Neodymium (III) Chromate(V)

Y. Aoki, H. Habazaki and H. Konno

Chemistry Letters, **33**, 992-993 (2004)

The novel sensing property of neodymium(III) chromate(V), NdCrO_4 , to methanol was demonstrated. The electric response of this compound did not rely on the surface potential change by the interaction with methanol gas, but was instead due to the redox interconversion of zircon-type NdCrO_4 to KDP-type $\text{NdH}_2\text{Cr}^{\text{III}}\text{O}_4$. The NdCrO_4 film prepared on alumina substrates with 2.5- μm thickness could respond to methanol of ppm order concentration with an apparent increase in electric resistance.

Formation of Platelet Structure Carbon Nanofilaments by a Template Method

H. Konno, S. Sato, H. Habazaki and M. Inagaki

Carbon, **42**, 2756-2759 (2004)

The formation of carbon nanofilaments by liquid phase carbonization of PVA and PVC was studied using Al templates of different topography. Carbon nanofilaments of several tens of nm in diameter could be formed using porous Al templates and liquid phase carbonization of polymer powders. As-formed porous anodic oxide films are useful as templates instead of filter types. The filaments had a platelet structure when the pore wall of the template was aluminum oxide.

Incorporation of Transition Metal Ions and Oxygen Generation during Anodizing of Aluminum Alloys

H. Habazaki, H. Konno, K. Shimizu, S. Nagata, P. Skeldon and G. E. Thompson

Corrosion Science, **46**, 2041-2053 (2004)

Enrichment of nickel at the alloy/film interface and incorporation of nickel species into the anodic film have been examined for a sputtering-deposited Al-1.2 at.% Ni alloy in order to assist understanding of oxygen generation in barrier anodic alumina films. Anodizing of the alloy proceeds in two stages similarly to other diluted aluminum alloys, for example Al-Cr and Al-Cu alloys, where the Gibbs free energies per equiv for formation of alloying element oxide exceed the value for alumina. In the first stage, a nickel-free alumina film is formed, with nickel enriching in an alloy layer, 2 nm thick, immediately beneath the anodic oxide film. In the second stage, nickel atoms are oxidized together with aluminum, with oxygen generation forming gas bubbles within the anodic oxide film. This stage commences after accumulation of about 5.4×10^{15} nickel atoms cm^{-2} in the enriched alloy layer. Oxygen generation also occurs when a thin layer of the alloy, containing about 2.0×10^{19} nickel atoms m^{-2} , on electropolished aluminum, is completely anodized, contrasting with thin Al-Cr and Al-Cu alloy layers on electropolished aluminum, for which oxygen generation is essentially absent. A mechanism of oxygen generation, based on electron impurity levels of amorphous alumina and local oxide compositions, is discussed in order to explain the observations.

Key Materials for Prevention of Global Warming and Steady Supply of Renewable Energy

K. Hashimoto, N. Kumagai, K. Izumiya, S. Meguro, K. Asami, H. Habazaki and M. Yamasaki

Materia, **43**, 318-325 (2004)

For prevention of global warming and running out of energy along with consumption of primary energy and emissions, global CO₂ recycling system is proposed. Included are H₂ production by solar energy-assisted seawater electrolysis by using Ni-C alloy cathodes and Mn oxide anodes, O₂ formation therein without Cl₂ formation, CO₂ methanation with the thus produced H₂ by using Ni-Zr catalysts.

Rf-GDOES Depth Profiling Analysis of a Monolayer of Thiourea Adsorbed on Copper

K. Shimizu, R. Payling, H. Habazaki, P. Skeldon and G. E. Thompson

Journal of Analytical Atomic Spectrometry, **19**, 692-695 (2004)

The 1st example of depth profiling anal., by radiofrequency-GDOES, of a layer of sub-nanometer thickness is presented. The example selected is that of a monolayer of thiourea adsorbed on a mirror-polished Cu substrate. The adsorbed layer is disclosed clearly in the depth profile as narrow peaks, above the Cu substrate, of C, H, N and S. Further, the positions of peaks are separated and located in the order that is expected from the orientation of the thiourea molecules adsorbed on the Cu substrate, the N peak was observed prior to the S peak.

Synthesis of Submicrometer-Sized β -SiC Particles from the Precursors Composed of Exfoliated Graphite and Silicone

H. Konno, T. Kinomura, H. Habazaki and M. Aramata

Carbon, **42**, 737-744 (2004)

Utilizing micro-spaces of exfoliated graphite (EG), a process to synthesize fine β -SiC particles was developed. Two types of low mol. wt. silicone and a catalyst were impregnated into EG by sorption, and then heated in air to cure the compounds. Formed precursors were black flakes of a few millimeters in diameter. Only by the heat treatment of precursors at 1500 °C for 5 h or at 1550-1600 °C for 1 h in Ar, β -SiC of a few tens to hundreds nanometers in size was obtained with the yield approximately 40 mass%. In the present process, EG play two important roles; one is as reaction spaces and the other is as a reductant that functions at elevated temperatures. Initially the cured silicone coats the graphite sheets of EG as thin films of <1 mm and, at >1300 °C it start to decompose and form small particles of a few tens to 100 nm in diameter on the graphite sheets. These intermediate particles are composed of the Si-C-O composites and SiO₂ and they spontaneously decompose to β -SiC from approximately 1400 °C and, at 1400-1500 °C the reduction of the remaining Si-C-O intermediates by graphite sheets occur and form well-crystallized fine β -SiC particles. The process is simple and raw materials are not expensive so that it is promising for industrial applications.

Synthesis of $\text{Sr}_2\text{FeMoO}_6$ by the Molybdic Acid Gelation Method and Its Magnetoresistance Effect

M. Ito, T. Takeda, H. Tamura, and S. Kikkawa

J. Jpn. Soc. Powder and Powder Metallurgy, **51**, 864-868 (2004)

Double perovskite $\text{Sr}_2\text{FeMoO}_6$ was prepared by combustion of gel prepared from an aqueous solution containing $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and Sr^{2+} and Fe^{3+} nitrates. The dried gel was pulverised and fired at 700°C for 6 h, and was fired again in an H_2/Ar (3%) flow for 3 h in the temperature range of $850\text{-}1000^\circ\text{C}$. The products slightly contaminated with impurities of $\alpha\text{-Fe}$ and FeMoO_4 were annealed at $1000\text{-}1200^\circ\text{C}$ in a sealed vacuum tube. The inner part of the sample annealed at 1100°C showed magnetoresistance effect of 8.3 % at room temperature. The amount of impurities did not change and the ordering of Fe^{3+} and Mo^{5+} enhanced by annealing. (Japanese)

Synthesis and Characterization of Hydrotalcite-ATP Intercalates

H. Tamura, J. Chiba, M. Ito, T. Takeda, and S. Kikkawa

Solid State Ionics, **172**, 607-609 (2004)

As a model for a drug delivery system, the intercalation of adenosine triphosphate (ATP) into hydrotalcite, a layered double hydroxide (LDH) of magnesium and aluminum, was studied. Well crystallized pure hydrotalcite with nitrate ions in the interlayer (LDH-NO₃) was formed by dropwise addition of a mixed solution of magnesium and aluminum nitrates to a sodium hydroxide solution. To intercalate ATP into hydrotalcite, LDH-NO₃ was put in an ATP solution at pH=7 (ion exchange method). It was found that interlayer nitrate ions were completely exchanged with ATP and that the interlayer distance doubled. Further, a mixed solution of ATP, magnesium, and aluminum ions was added dropwise to a sodium hydroxide solution (coprecipitation method) and it was found that the product contains ATP. (English)

(ZnO)₃In₂O₃ Fine Powder Prepared by Combustion Reaction of Nitrates-Glycine Mixture

S. Kikkawa, H. Sasaki, H. Tamura, S. Hosokawa, and H. Ogawa

Minerals Research Bulletin, **39**, 1821-1827 (2004)

Conducting Zn-In-O system fine powder was obtained by combustion of gel prepared from an aqueous solution containing zinc and indium nitrates and glycine. Glycine acts as a gelling agent as well as a fuel in the combustion with nitrates as strong oxidizing agents. At a low furnace temperature of 350°C, (ZnO)₃In₂O₃ which cannot be formed below 1260°C by a solid state reaction between ZnO and In₂O₃ was obtained. The combustion synthesis led to agglomerates of fine powders of hexagonal platelets of about 40 nm in diameter. Its compacted mass showed an electrical resistivity of about 700 Ωcm. The degree of agglomeration of the product decreased by dispersing it in an acetic acid aqueous solution.. (English)

Effect of Far-Infrared Light Irradiation on Water as Observed by X-Ray Diffraction Measurements

S. Shimokawa, T. Yokono, T. Mizuno, H. Tamura, T. Erata, and T. Araisō

Japanese Journal of Applied Physics, **43**, L545-L547 (2004)

X-ray diffraction measurements were made on water irradiated with far-infrared (FIR) light. It was found that the X-ray diffraction intensity at a 2θ angle of 30° increased by about 2 times with the irradiation. The increase in the X-ray diffraction intensity was interpreted in terms of the destruction of water clusters. (English)

Theorization on Ion-Exchange Equilibria -Activity of Species in 2-D Phases-

Hiroki Tamura

J. Colloid Interface Sci., **279**, 1-22 (2004)

This paper describes the modeling of ion-exchange equilibria for hydroxyl sites on metal oxides and carboxyl sites in resins by applying the Frumkin equation containing equilibrium and interaction constants. The formation of bonds between ions and exchanger sites was evaluated by the equilibrium constant and the suppression of bond formation due to electrostatic, geometric, and other lateral interactions between ions was evaluated by the interaction constant. It was established that the properties of ions are determined by the valence, size, and hydration state of the ions. For alkali metal ions, the hydrated ion diameter decreases with atomic number, and the adsorption affinity and repulsive interaction of the ions increase in the same order. The affinity of divalent transition metal ions coincides with that for hydroxo complex formation in solution. The properties of exchangers are explained by the molecular and pore environments around the functional groups. The acid-base nature of oxide surface-hydroxyl sites is determined by the electronegativity of surrounding lattice metal ions. The acid strength of resin carboxyl sites is determined by the electron repelling effect of adjacent methyl groups. Metal oxides have internal surfaces due to pores, crevices, flaws, etc. Within pores the suppression is large because of repulsion from ions adsorbed on opposite pore walls (across-pore interaction). Ion-exchange resins have nanopores as the spaces between polymer chains and also macropores as the voids from where solvent droplets have evaporated. Ions are differentiated by pore sizes that can access or not access sites on the internal surfaces of the pores. The ion-exchange reactivity in pores smaller than the hydrated ion diameters is small because dehydration energy is necessary before the ions enter into the pores, and the suppression is also small because of a small polarization of dehydrated ion-charged site pairs. In wide pores larger than hydrated ions, the bond formation is easier, but the suppression is larger because of a larger polarization of hydrated ion-charged site pairs and also of the across-pore interaction. Finally, this paper attempts a formulation

of activity coefficients of exchanging sites and adsorbed ion-site pairs, and compares the proposed activity coefficients of interphase species with that of solution species given by the Debye-Hückel equation. (English)

The Mechanical Properties of TiAl Alloy Coated by a Two-step Cr and Al Diffusion Treatment

T. Nishimoto, T. Izumi and T. Narita

Report of the 123rd committee on high temperature metals and alloys, Japan Soc. for Promotion of Science, 45 (2004), p. 213-219 .

The effects of coatings on the creep and oxidation behavior of Ti-50Al alloy were investigated at 1173K in air at a constant loading of 30MPa. The coating was formed by a two-step Cr/Al diffusion treatment and consisted of an outermost TiAl₂ layer, an outer Al-rich γ layer, an intermediate γ , Laves and β mixture layer, and a Cr diffusion zone. Creep tests were also carried out with sole Cr or Al coated TiAl and also of uncoated TiAl. The oxide scales formed on the uncoated TiAl and the sole Cr coated specimens were a mixture of TiO₂ and Al₂O₃, which displayed several exfoliations. Both the two-step Cr/Al coated TiAl and the sole Al coated specimens formed a protective Al₂O₃ 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.

Effects of Platinum on the Interdiffusion and Oxidation Behavior of Ni-Al-Based Alloys

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Materials Science Forum, **461-464**, 213-222 (2004)

Thermal barrier coating (TBC) systems, needed for higher thrust with increased efficiency in gas turbines, typically consist of an alumina-scale forming metallic bond coat and a ceramic topcoat. The durability and reliability of TBC systems are critically linked to the oxidation behavior of the bond coat. Ideally, the bond coat should oxidize to form a slow-growing, non-porous and adherent thermally grown oxide (TGO) scale layer of α -Al₂O₃. The ability to promote such ideal TGO formation depends critically on the composition and microstructure of the bond coat, together with the presence of minor elements (metal and non-metal) that with time diffuse into the coating from the substrate during service. An experimental program was undertaken to attain a more detailed fundamental understanding of the phase equilibria in the Ni-Al-Pt system and the influences of alloy composition on the formation, growth and spallation behavior of the resulting TGO scales formed during isothermal and thermal cycling tests at 1150°C. Additional studies were conducted to determine the influence of platinum on interdiffusion behavior in the Ni-Al system, and how this influence would impact coating/substrate interdiffusion. It will be shown that platinum has a profound effect on the oxidation and interdiffusion behaviors, to the extent that novel advanced coating systems can be developed.

Numerical Analysis of the Production Process of Composite Layer by Using Double Casting Method

K. Ohsasa and K. Matsuura

Function Graded Materials (FGM) 2003, 275-280, (2004)

A new casting method named a double casting method was investigated to produce an ingot composed of multi-layers with different compositions. The unsolidified core of a solidifying ingot was replaced with another molten alloy during solidification process. A numerical analysis of the double casting process was carried out and the condition for an obtaining good joining between composite layers was examined in relation to the compositions of the layers. The numerical analysis showed that to obtain a good joining, the interface between the composite layers should be held over 5 seconds under the such condition as fraction solid is less than 0.3. (Japanese)

Phase-field Simulation of Temperature Gradient Transient Liquid Phase Diffusion Bonding

Y.Natsume, K.Ohsasa and T.Narita

Function Graded Materials (FGM) 2003, 315-320, (2004)

A numerical simulation of the temperature gradient transient liquid phase diffusion bonding (TG-TLP) was carried out by a phase-field method. The bonding time of the TG-TLP is shorter than that of conventional TLP diffusion bonding, because solidification is controlled by diffusion in liquid. In this simulation, it was found that the bonding time decreased with increasing the temperature gradient imposed in the bonding system, however, the bonding zone (segregation zone) became wide. It was found that the thickness of an insert metal and equilibrium partition coefficient also affected the bonding time. The bonding time remarkably decreased with increase in the partition coefficient of solute element in the insert metal. (Japanese)

Fabrication of Grainrefined Nb-Al-Si Ternary Alloy and Evaluation of Its Properties

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Function Graded Materials (FGM) 2003, 183-188, (2004)

A multiphase intermetallic Nb-Al-Si ternary alloy with NbAl₃ phase and Nb₅Si₃ phase was produced by Self-propagating High Temperature Synthesis (SHS). The SHS-ed alloy was crushed by milling, and then was sintered by the Spark Plasma Sintering (SPS) method. An average crystal grain size of an SPS-ed alloy was reduced to 0.6 micrometers when the alloy was ball milled for 36hours and then bead milled for 10 hours. The hardness and bending strength of the SPS-ed alloy increased remarkably due to the grain refinement. The Vickers hardness of the as-SHS-ed alloy was 860. However, it increased to 14 20 due to the grain refinement. The bending strength of the as-SHS-ed alloy could not be measured because the bend test could not be performed due to its fatal brittleness. However, the SPS-ed alloy with the fine grains exhibited a fracture strength of 210MPa. (Japanese)

Estimation of Grain Boundary Properties in bcc Iron by Molecular Dynamics Simulation

K. Ohsasa, T. Toyama, K. Kurokawa and K. Matsuura

Proc. of the 4th Int. Conf. on Physical and Numerical Simulation of Materials Processing (2004)

A molecular dynamics simulation was carried out to study the grain boundary properties such as the grain boundary energy and the grain boundary strength in bcc iron. To make a grain boundary, two grains having different crystallographic orientations were contacted in the simulation. An empirical pair-potential and a semi-empirical embedded atom method (EAM) were used in the simulation. The grain boundary energies for various crystallographic orientations were calculated from the configurations of the iron atoms at the grain boundaries. The calculated grain boundary energies for [001] symmetric tilt and [001] twist grain boundaries increase with increase in tilt and twist angles, but exhibited low energies at the special angles correspond to the coincidence grain boundaries. The grain boundary energy calculated with the EAM potential was small in comparison with the calculated grain boundary energy with the pair-potential. The effect of grain boundary segregation of phosphorous on the grain boundary properties was examined and it was shown that the grain boundary energies with phosphorus segregation were shifted to lower values. An atomistic tensile test simulation for a grain boundary was carried out, and the grain boundary strength for various crystallographic orientations was evaluated. The fracture stress for [001] symmetric tilt grain boundary changed with the change in tilt angle, and exhibited higher values at the coincidence grain boundaries. The fracture strength of the grain boundary with phosphorous segregation exhibited the lower value than that without segregation.

A Role of Vaporization of Metal Oxide in Formation of SiO₂ Scale on Metal Disilicides

K.Kurokawa, K.Ohsasa and K.Matsuura

Proc. of the 4 th Int. Conf. on Physical and Numerical Simulation of Materials Processing (2004)

It is well known that some metal disilicides, for example MoSi₂ and WSi₂, show excellent oxidation resistance at high temperatures. Therefore, these disilicides are being considered as promising materials for applications in oxidizing environments at ultra-high temperatures.

The excellent oxidation resistance of the disilicides is due to the formation of a protective SiO₂ scale. When a metal oxide formed as an oxidation product possesses a high vapor pressure, the vaporization often plays an important role in the formation of a protective SiO₂ scale. That is to say, as a consequent of simultaneous formation of metal and silicon oxides at an early stage of oxidation and subsequent evaporation of the metal oxide, only SiO₂ may remain on the disilicide substrate. The vapor pressures of MoO₃, V₂O₅, WO₃, and Re₂O₇ are very high, and the high vapor pressure must be advantageous for forming a SiO₂ scale.

In the present study, oxidation tests of WSi₂ and ReSi_{1.75} were carried out in air at temperatures ranging from 773 to 1773 K. Based on the results, a relationship between vapor pressure of metal oxide and formation of SiO₂ scale was clarified. Namely, when the vapor pressure of metal oxide reaches 10 Pa, a SiO₂ scale forms on the disilicides. The vapor pressure of 10 Pa corresponds to about 473 K in ReO₃, 1073 K in MoO₃, 1173 K in V₂O₅, and 1673 K in WO₃.

Reactive NiAl Coating of Fe-base Alloys

K.Matsuura, K.Ohsasa, K.Kurokawa, and M.Kudoh

Proc. of the 4 th Int. Conf. on Physical and Numerical Simulation of Materials Processing (2004)

A new process for coating of Fe-base alloys with a corrosion resistant intermetallic NiAl has been proposed, and its feasibility has been investigated using a simple experiment and a numerical simulation. The coating process is based on an exothermic reaction between Ni powder and Al droplets. In the experiment, when an Al droplet was dropped onto Ni powder that had been placed on a surface of an Fe-base alloy, the droplet and powder exothermically reacted and produced a bead of liquid NiAl on the surface of the alloy. The heat from the liquid NiAl melted the surface of the Fe-base alloy, and after solidification the alloy was coated with NiAl. In the numerical simulation, the change in temperature distribution with time was out-putted on the display, and the maximum depth of the melted base metal was monitored. The depth increased as the initial temperatures of the powder, droplet and the base metal increased. On the other hand, the depth decreased as the thickness of the base metal increased. The depth was also affected by the thermal properties of the base metal; it decreased with increasing melting point, specific heat, latent heat and thermal conductivity of the base metal.

Numerical Simulation of Dendrite Growth of Binary Alloys with Fluid Flow by Using Phase-field Method

Y. Natsume, K. Ohsasa and T. Narita

Proc. of the 6th Pacific Rim International Conference on Modeling of Casting and Solidification Processing 2004 ,14 9 -155 (2004)

Numerical simulation of the dendrite growth of an Fe-0.15mass%C binary alloy under fluid flow was carried out by using two-dimensional phase-field method, and the dendrite deflection in the alloy system was investigated. The flow pattern in a solidifying alloy was calculated by solving the Navier-Stokes equation and the effect of fluid flow was incorporated into the phase-field calculation by adding the movement of solute in liquid due to fluid flow. The mechanism of the dendrite deflection due to fluid flow was examined based on the simulated results and it was shown that the change in the solutal field is the main factor responsible for the deflection of a dendrite in an alloy system. The simulation also showed that the deflection angle of a single dendrite was small, and the large deflection angles of grains observed in the experiments were thought to have been caused by nucleation or fragmentation in front of the dendrites and the subsequent competitive growth.

Molecular Dynamics Simulation of Solidification of Iron

K.Ohsasa, Y.Natsume, H.Yasumoto and K.Matsuura

Proc. of the 66th World Foundry Congress, 34 5-355 (2004)

A molecular dynamics simulation was carried out to study the solidification process of molten iron in atomistic scale. In the simulation, liquid iron was contacted with a virtual nucleation catalyst and the subsequent heterogeneous nucleation process of iron was investigated. The nucleation rate was changed with both changes in the degree of undercooling and the interfacial energy between the molten iron and the nucleation catalyst. The growth velocity of a nucleated solid was estimated for different crystallographic orientations and the kinetic coefficient of the moving solid-liquid interface was evaluated. The evaluated kinetic coefficient was used for estimating the mobility parameter used in the phase-field method. A phase-field simulation for the evolution of the dendrite morphology in an Fe-C binary system was carried out and the effectiveness for combining the molecular dynamics method with the phase-field method was confirmed.

Numerical Simulation of Macrostructure Evolution in Al Base Multi-component Alloys Using a New Model coupled Cellular Automaton Method with Phase-field Method

Y. Natsume, K. Ohsasa and T. Narita

Proc. of the 66th World Foundry Congress, 333-343 (2004)

A new simulation model for the evolution of micro-macro structure of alloys during solidification has been developed. In this model, the cellular automaton method for calculating macrostructure evolution was coupled with the phase-field method for calculating microstructure evolution (PF-CA model). The growth kinetics of dendrite tips, i.e., the undercooling vs. growth velocity relationship of dendrite tips, was evaluated by phase-field calculations. The obtained growth kinetics was applied to the cellular automaton model instead of the commonly used KGT model. The developed model was used for simulation of the evolution of macrostructures of Al-Si binary and Al-base multi-component commercial alloys. The simulation could produce the macrostructures similar to experimentally observed macrostructures.

Application of Reactive Casting to Coating and Joining of Aluminide Intermetallics

K. Matsuura, M. Kudoh, Y. Miyamoto and K. Ohsasa

Proceedings of the 66th World Foundry Congress, (2004),135-14 5.

When droplets of aluminum liquid are dropped onto nickel powder placed on a base metal such as steel, the aluminum and nickel exothermically react and produce nickel aluminide intermetallics and the base metal is coated with the aluminide intermetallics. When the aluminum liquid is dropped onto nickel powder placed in the root gap made between two NiAl plates, the plates are welded.