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INTERFACIAL ELECTROCHEMISTRY LABORATORY
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BIOMEDICAL, DENTAL MATERIALS AND ENGINEERING
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DISSIMILAR MATERIALS INTERFACE ENGINEERING
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Assoc Prof. Dr. Hiroki Tamura

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Electrode and Their Electron Transfer Activity

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Selective formation of porous layer on n-type InP by anodic etching combined with scratching

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Improvement of Oxidation Resistance of NbSi₂ by Addition of Boron

Oxidation behavior of sulfidation processed TiAl-2at.%X(X=Si, Mn, Ni, Ge, Y, Zr, La and Ta) alloys at 1173K in air

α -NiPt(Al) and Phase Equilibria in the Ni-Al-Pt System at 1150°C

Interdiffusion Behavior of Pt-modified γ -Ni + γ' -Ni₃Al Alloys Coupled to Ni-Al-based Alloys

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Dissolution Resistance of Rusts on Galvanized Steels in Atmospheric Environments

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

Research programs in progress are as follows:

(1) New corrosion resistive films consisting of conductive polymers

A conductive polymer coating was applied to corrosion prevention of carbon steels. A bilayered polypyrrole (PPy) film doped by molybophosphate (MoP) ions at the inner layer and by organic ions at the outer layer was electrochemically formed on the steel plate in aqueous solution containing pyrrole monomer. The MoP ions doped in the inner layer functions as accelerator of passive oxide film between the PPy layer and substrate steel. The large organic anions doped in the outer layer suppresses leaching of the MoP into aqueous solutions. The corrosion protection of the layer was tested by immersion of the PPy-coated steel in aqueous

NaCl solution. The passivity of the steel was maintained for time period longer than 100 h, where appreciable corrosion was not observed. The PPy film was also prepared on zinc from tartrate solution containing sodium molybdate and pyrrole monomer. Before formation of the PPy film, a salt layer consisting of zinc tartrate and zinc molybdate is initially formed on the substrate zinc, the layer which works as a passivation layer for zinc.

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

Corrosion products on zinc layer coupled with bare steel in atmosphere were studied by Raman spectroscopy. At the presence of NaCl precipitate, zinc-hydroxy carbonate and zinc-hydroxy chloride were observed on both surface of zinc layer and bare steel. The formation of zinc-hydroxy chloride depended on concentration of ZnCl_2 in aqueous layer in which Zn^{2+} was initially formed from a reaction of $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$ coupled with oxygen reduction on bare steel surface.

(3) Corrosion and passivation of Nd magnets

Corrosion behavior of Nd magnets was studied in NaCl solution. The concentration of O_2 in the solution greatly affects the corrosion rate of Nd magnets. Passivation of Nd magnets was also investigated in neutral borate solution at PH 8.4 by ellipsometry and GD-OES. The thickness of the passive oxide film anodically formed is found to be linearly proportional to potential. The growth of the film may be followed by the ionic migration mechanism under high electric field proposed by Cabrera and Mott.

(4) Adsorption of MPSA and PEG on copper electrode

Adsorption of 3-mercaptopropionic acid (MPSA) and polyethylene glycol (PEG) on copper was investigated in perchloric acid solution by in-situ surface-enhanced infrared absorption spectroscopy (SERAS). The adsorption intensity of the organic compounds was determined and orientation of the adsorbed species was discussed.

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

BiTe was electrodeposited in AlCl_3 -NaCl-KCl molten salt containing BiCl_3 and

TeCl₄ at 423K. Stable deposition of pure Bi and pure Te were not obtained by the electrolysis, because electrodeposited Bi and Te dissolved into the molten salt immediately. Pure Sb, Bi-Te ally, and Bi-Sb alloy were successfully electrodeposited in the melt containing BiCl₃ and/ or SbCl₃. The composition of Bi-Te and Bi-Sb depended on electrolysis potential between 0.8 and 1.0V vs. Al/Al³⁺.

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

To remove the Mg content in Al alloy, a reactive filter of ZnMn₂O₄ synthesized from the used dry battery materials was prepared. Metallic Mg reacted with ZnMn₂O₄ to produce MgMn₂O₄ at 1073K. Mg concentration in the Al alloy decreased from 6 to 1 at% after the filtration.

Other Activities

Prof. Ohtsuka attended the 56th Annual Meeting of ISE, Busan/Korea, Sept. 25-30, 2005, and presented a paper entitled by "Polypyrrole Coating Doped by PMo₁₂O₄₀³⁻ for Corrosion Prevention of Steels". Dr. Ueda attended the 7th International Symposium on Molten Salt Chemistry & Technology, Toulouse/France, Aug. 27-Sept.2, 2005, and presented a paper entitled by "Reduction of SiO₂ to Si by Aluminum Particles in NaCl-KCl-AlCl₃ Molten Salt". He also attended the International Symposium on Electrochemical Processing of Tailored Materials, Kyoto/Japan, Oct. 3-5, 2005, and presented a paper entitled by "Electrochemical Study of Sb, Bi and Te in AlCl₃-NaCl-KCl Molten Salt".

Presentations

Relation between AC capacitance and potential modulations reflectance on passive film of stainless steel, Y. Sasaki and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 20-21, 2005.

Reduction of SiO₂ to Si by aluminum metallic fog in molten salt, Y. Abe, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ,

Muroran Institute of Technology, Muroran, January 20-21, 2005.

Surface enhancement infrared spectroscopy of organic compounds on copper electrode, M. Yasuda, T. Sasaki, M. Oosawa and T. Ohtsuka Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 20-21, 2005.

Corrosion protection of mild steel covered by the composite film of molybdophosphate and polypyrrole, M. Iida, M. Ueda and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, February 1-2, 2005.

Change of amount of Cu corrosion products with corrosion environment, Y. Horiguchi, T. Sasaki and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, February 1-2, 2005.

Corrosion reaction of zinc for formation of zinc hydroxi-chloride, 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., Hokkaido University, Sapporo, February 1-2, 2005.

Characterization of rust layer on weathering steel, T. Ohtsuka, 36th technical seminar of Jpn. Soc. of corros. eng., Tokyo University of Science, Tokyo, February 2, 2005

Passivation and corrosion protection of mild steel covered by conductive polypyrrole film, T. Ohtsuka, M. Iida and M. Ueda, Electrochemical Society of Jpn, Faculty of Engineering, Kumamoto University, Kumamoto, April 1-3, 2005

Reduction of SiO₂ to Si by aluminum metallic fog in Molten Salt, M. Ueda, Y. Abe and T. Ohtsuka, Electrochemical Society of Jpn, Faculty of Engineering, Kumamoto University, Kumamoto, April 1-3, 2005

Investigation of analysis method on structure of Fe passive film by grazing incident X-ray scattering at Spring-8, M. Sato, M. Yamashita, S. Fujimoto, H. Konishi, M. Kimura, Y. Tabira, T. Doi, T. Kamimura, M. Nagoshi, S. Suzuki, T. Nakayama, T. Ohtsuka, Japan Society of Corrosion Engineering, Materials and Environments 2005, Keio University, Yokohama, May 26-28, 2005

Availability of Synchrotron Radiation for Corrosion Engineering, T. Ohtsuka, 151st symposium on corrosion engineering, Jpn. Soc. of corros. eng., Chuo Univ., Tokyo, June 17, 2005

Co-deposition of Al-Cr-Ni alloys in AlCl₃-EMIC ambient temperature molten salt, M. Ueda, H. Ebe and T. Ohtsuka, 1st International Congress on Ionic Liquids (COIL), Salzburg Congress, Salzburg, Austria, June 19-22, 2005

Atomic-Structure Characterization of Passive Film of Fe by Grazing Incident X-ray Scattering at Spring-8, Masugu Sato, Masao Kimura, Masato Yamashita, Hiroyuki Konishi, Shinji Fujimoto, Yasunori Tabira, Takashi Doi, Masayasu Nagoshi, Shigeru Suzuki, Takayuki Kamimura, Takenori Nakayama and Toshiaki Ohtsuka, The 9th International Symposium on the Passivation of Metals and Semiconductors, and the Properties of Thin Oxide Layers, Paris, June 27-30, 2005

Removal of alloy elements from liquid aluminum alloy by filtration process -Investigation of filtration process-, H. Takahashi, T. Uchiyama, M. Yoshida, S. Hirano, M. Ueda, Y. Shibata, T. Takashima, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 14-15, 2005

Removal of alloy elements from liquid aluminum alloy by filtration process -Behavior of intermetallic compounds of Si and Fe in liquid aluminum-, T. Takashima, Y. Shibata, M. Ueda, H. Takahashi, T. Uchiyama, M. Yoshida, S. Hirano, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 14-15, 2005

Removal of alloy elements from liquid aluminum alloy by filtration process -Investigation of calcium carbonate from scallop as a filter material-, Y. Shibata, M. Ueda, T. Takashima, H. Takahashi, T. Uchiyama, M. Yoshida, S. Hirano, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 14-15, 2005

Removal of alloy elements from liquid aluminum alloy by filtration process -Molten salt treatment of used filter containing aluminum metal-, M. Ueda, T. Takashima, Y. Shibata, H. Takahashi, T. Uchiyama, M. Yoshida, S. Hirano, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran Institute of Technology, Muroran, July 14-15, 2005

Protection treatment of Nd magnet using a phosphate and molybdate, Y. Nunoko and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 14-15, 2005

Electrochemical study of Sb and Bi in chloride molten salt, H. Ebe, M. Ueda and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, July 14-15, 2005

Behavior of additives of Cu plating on electrode, M. Yasuda, T. Sasaki, M. Oosawa and T. Ohtsuka, Summer Meeting of Hokkaido Branch of Jpn chem. soc., Future University-Hakodate, Hakodate, July 23-24, 2005

In-situ IR spectroscopy in the initial stage of atmospheric corrosion, T. Sasaki, Hokkaido summer seminar 2005, Hokkaido University, Sapporo, August 5, 2005

Reduction of SiO₂ to Si by aluminum particles in NaCl- KCl-AlCl₃ molten salt, M. Ueda, Y. Abe and T. Ohtsuka, 7th International Symposium on Molten Salts Chemistry & Technology, Universite Paul Sabatier, Toulouse, France, August 27-September 2, 2005

Hydration and dehydration of passive film under anodic electric fields, T. Ohtsuka

and Y. Sasaki, fall meeting of ECSJ 2005, Chiba University, Chiba, September 8-9, 2005

Behavior of additives of Cu plating on electrode, M. Yasuda, T. Sasaki, M. Oosawa and T. Ohtsuka, fall meeting of ECSJ 2005, Chiba University, Chiba, September 8-9, 2005

AC response of stainless steel covered with passive film –complex capacitance and potential modulation reflectance-, T. Ohtsuka and Y. Sasaki, 52nd Japan Conference on Materials and Environments, Hokkaido University, Sapporo, September 14-16, 2005

Relation between growth of rust layer on weathering steel and wet time period, T. Ohtsuka, Y. Sato and M. Ueda, 52nd Japan Conference on Materials and Environments, Hokkaido University, Sapporo, September 14-16, 2005

Electrodeposition of Al alloy in ambient temperature and low temperature molten salt, M. Ueda and T. Ohtsuka, 52nd Japan Conference on Materials and Environments, Hokkaido University, Sapporo, September 14-16, 2005

Polypyrrole coating Doped by $\text{PMo}_{12}\text{O}_{40}^{3-}$ for corrosion prevention of steels, T. Ohtsuka, M. Iida and M. Ueda, The 56th Annual Meeting of the International Society of Electrochemistry, Busan, Korea, September 25-30, 2005

Electrochemical study of Sb, Bi and Te in $\text{AlCl}_3\text{-NaCl-KCl}$ molten salt, H. Ebe, M. Ueda and T. Ohtsuka, International Symposium on Electrochemical Processing of Tailored Materials, The Kyoto University Clock Tower Centennial Hall, Kyoto, October 3-5, 2005

Behavior of additives on Cu electrode, M. Yasuda, T. Sasaki, M. Oosawa and T. Ohtsuka, The 112th Annual Meeting of Surf. Finish. Soc. Jpn., Kanazawa, October 5-7, 2005

Polypyrrole coating for corrosion prevention of steels, Damian Kowalski,

Corrosion Dream 2005- Young Scientist Seminar, Osaka University, Osaka, November 22, 2005

Al-Cr alloy electroplating on TiAl using a molten salt electrolysis, M. Ueda, Corrosion Dream 2005- Young Scientist Seminar, Osaka University, Osaka, November 22, 2005

Electrodeposition of Bi-Sb and Bi-Te alloys from chloride molten salt, H. Ebe, M. Ueda, T. Ohtsuka, The 37th Symposium on Molten Salt Chemistry, Keio University, Yokohama, November 24-25, 2005

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-indentation in solution for the passive nickel (111) and (110) surfaces

Single-crystal Ni (111) or (110) disc plate with a diameter of 10 mm and a thickness of 2mm was used for experiments. The Ni specimen was mechanically polished with diamond paste, ultrasonically washed in ethanol and finally electropolished in a mixed solution of $\text{HClO}_4 + 70\% \text{CH}_3\text{COOH}$ at 1.5 A cm^{-2} for 2s. The Ni specimen was potentiostatically passivated at 0.0 V or 1.0 V (SHE) for 1 h in pH 8.4 borate solution. The nano-indentation was performed under a maximum load of $L_{\text{max}} = 25 - 200 \mu\text{N}$ for the passive Ni surface kept at 0.0 V or 1.0 V (SHE) in pH

8.4 borate solution. The nano-indentation in air after passivation of the Ni specimen was also performed to compare the results obtained with nano-indentation in solution and in air. Any differences in hardness between the passive Ni (111) and (110) surfaces were not observed within experimental errors. The value of hardness obtained with nano-indentation at 0.0 V or 1.0 V (SHE) in solution was always larger than that obtained in air after passivation.

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

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

(3) Application of Resistometry to Corrosion Monitoring of Cu wire.

Carbon steel, titanium and copper have been considered as candidates for repository of high level radio active nuclear waste produced in power plant. Resistometry was thus applied to evaluate corrosion behavior of Cu in underground environment. Two Cu wires of 0.1 mm in diameter were used as corrodible sample and reference resistance to reduce influence of temperature fluctuation, respectively. Electric resistance of corroding Cu was monitored in the solution in contact with bentonite clay at 353 K. Corrosion rate was around $2\text{-}3 \text{ pm s}^{-1}$ and was considerably higher than that previously reported. Generally anodic oxidation reaction of Cu is coupled with cathodic reduction reaction of oxygen dissolved in the solution and thus the discrepancy of corrosion rate in the current study and the previous report was probably due to existence of residual oxygen in the system whose contribution is

relatively large for Cu wire electrode with very small surface area used in this study. SEM observation showed that the surface of Cu wire was covered with film of corrosion products composed of Cu oxide and carbonate. This film was electrically conductive and photoelectrochemically active due to its p-type semiconductive property. Dissolution of Cu substrate beneath the film was accelerated by cathodic reaction occurring on electroconductive film resulting in formation of void between corrosion film and Cu substrate.

(4) Effect of Copper Pretreatment on Double Zincate Process of Al-Si Alloy Films

Uniform plating on Al-Si alloys has been desired for manufacturing of electronic devices such as lead frame used in LSI. Ordinary double zincate pretreatment on Al-Si alloy, however, results in nonuniform Zn deposition probably due to nonuniform composition of Si on the surface. Etching pretreatment in $\text{H}_2\text{SO}_4 + \text{CuSO}_4$ solution was applied to magnetron sputter deposited Al-Si alloy films formed on glass plate to improve uniformity of Zn deposition in double zincate process. In the etching process small amount of Cu deposited on alloy surface accompanying with Al dissolution. These deposits acted as nucleation sites for Zn deposition in zincate process and thus provided uniform, fine and thin Zn layer on Al-Si alloys. This effect was prominent on alloys containing 2.0 or 2.6 atomic % of Si comparing with those containing 0 or 1.0 atomic % of Si. Such discrepancy was probably caused by efficient Cu deposition on alloys with relatively higher Si concentration.

(5) Development of Monitoring System using Multiple Electrodes to Evaluate Spatial Distribution of Corrosion Rate

Corrosion monitoring system was developed which enables evaluation of spatial distribution of polarization current and immersion potential of corroding metals. In this system corrodible material is divided into a few to several pieces and reconstructed to reproduce the corroding condition. These electrodes are connected to the circuit in which these electrodes were imaginarily grounded, i.e., all electrodes are kept in a same potential and the polarization current of each electrode can be measured individually. This means that contribution of anodic or cathodic current of individual part to a whole corroding materials can be quantitatively analyzed. This system can be applied to many kinds of nonuniform corrosion such as crevice corrosion, galvanic corrosion, and so on. Equipment was constructed with

combination of operational amplifiers, photo-MOS relays, data acquisition board installed in a computer and control software. The system was applied to corrosion monitoring of welding materials and the distribution of anode / cathode contribution around welding area and their transition with immersion time was analyzed.

Other Activities

In April, Prof. M. Seo was invited to the JSPS Bonn Symposium, Bonn, Germany and presented the lecture entitled “Mechanical and Chemical Interactions of Passive Metal Surfaces Evaluated by Nano-indentation or Nano-scratching in Aqueous Solution”. He was also invited to Tribocorrosion Seminar at the Max-Planck Institute for Iron Research, Duesseldorf and presented the lecture entitled “Mechanical Properties of Passive Metal Surfaces Measured by Nano-indentation and Nano-scratching in Solution”.

In June, Prof. M. Seo, Dr. K. Fushimi and Mr. D. Kawamata participated in the 9th International Symposium on the Passivation of Metals and Semiconductors and the Properties of Thin Oxide Layers (PASSIVITY-9), Paris, France and Prof. M. Seo presented the keynote lecture entitled “Differences in Mechanical Properties of the Passive Metal Surfaces Obtained in Solution and Air”.

In September, Prof. M. Seo organized ‘International Symposium on "Progress in Corrosion Research" in Commemoration of Centenary of Birth of Professor Go Okamoto’ at Hokkaido University and lectured “Changes in Mass and Stress during Anodic Oxidation and Cathodic Reduction of the Cu/Cu₂O Multilayer Film”. Prof. M. Seo, Assoc. Pro. K. Azumi, Dr. K. Fushimi, Ms. M. Nakajima, and Mr. A. Naganuma participated in the 56th Annual Meeting of the International Society of Electrochemistry, Busan, Korea and Prof. Seo presented the lecture entitled “Nano-scratching in Solution to the Ta(100) Surface Subjected to Anodic Oxidation”.

In October, Prof. M. Seo and Assoc. Prof. K. Azumi participated in the 208th ECS Meeting, Los Angeles, USA, to present the lecture entitled “Local Cathodic Corrosion of n-type InP (001) by Scratching” and “MO Simulation of Surface Diffusion of Zinc Adatoms on Zinc Surface”, respectively.

The following foreign scientists visited this laboratory: Mr. S. -I. Cho and Mr. J. -S. Kim (Ph.D. Students of Prof. S. -I. Pyun), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST),

Korea, from January 31 to February 3, Prof. R. Oltra, Laboratoire de Recherches sur la Réactivité des Solides, Université de Bourgogne, France, September 2 to 21. Dr. A. Bund, Technische Universität Dresden on November 11. Furthermore Mr. H. H. Elsentreicy joined as a Ph.D. Student Candidate from October 2.

Presentations

M. Hagioi, M. Seo; Mechanism of Anodic Oxidation and Cathodic Reduction of the Cu/Cu₂O Multilayers, The 2005 Joint Meeting of Hokkaido Section of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Corrosion Eng., Sapporo, Feb. 1-2, 2005.

D. Kawamata, M. Seo; Nano-scratching in Solution to the Ta (100) Surface Anodically Oxidized at a Constant Potential, *ibid.*

K. Takase, K. Fushimi, M. Seo; Current Transients from Passive Iron by Micro-indentation in Solution, *ibid.*

M. Nakajima, K. Azumi, M. Seo; Corrosion Behavior of Ti Wire in Acidic and Alkaline Solutions using Resistometry, *ibid.*

A. Naganuma, K. Fushimi, M. Seo; Fabrication of Microelectrode by Use of Electroless Plating, *ibid.*

A. Naganuma, K. Fushimi, M. Seo; Fabrication of Microelectrode by use of Electroless Nickel Plating, The 111th Annual Meeting of Surf. Finish. Soc. Jpn., Narashino, Mar. 14-16, 2005.

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

M. Nakajima, K. Azumi; Evaluation of Corrosion Rate of Ti in Acidic Solution using Resistometry, *ibid.*

K. Azumi, M. Seo; Formation of Small Cu Deposition using Thin Glass Tube, *ibid.*

K. Fushimi, K. Azumi, M. Seo; Excess Current Flow through Microelectrode Vibrating in the Vicinity of Surface, *ibid.*

M. Seo; Mechanical Properties of Passive Metal Surfaces Measured by Nano-indentation and Nano-scratching in Solution, Tribocorrosion Seminar, Duesseldorf, Germany, Apr. 19, 2005.

M. Seo; Mechanical and Chemical Interactions of Passive Metal Surfaces Evaluated by Nano-indentation or Nano-scratching in Aqueous Solution, The JSPS Bonn Symposium, Bonn, Germany, Apr. 22-23, 2005.

K. Fushimi, K. Takase, M. Seo; Current Transients due to Rupture and Repair of Passive Film during Micro-indentation in Solution, The 2005 Annual Meeting of Jpn. Soc. Corros. Eng., Yokohama, May. 26-28, 2005.

K. Azumi, M. Nakajima, M. Seo; Repassivation of Scratched Ti, *ibid.*

M. Seo, D. Kawamata, M. Chiba; Differences in Mechanical Properties of the Passive Metal Surfaces Obtained in Solution and Air, The 9th International Symposium on the Passivation of Metals and Semiconductors and the Properties of Thin Oxide Layers (PASSIVITY-9), Paris, France, Jun. 27-Jul. 1, 2005. (Keynote lecture)

K. Fushimi, K. Takase, M. Seo; Current Transients of Passive Iron during Micro-indentation in Solution, *ibid.*

D. Kawamata, M. Seo; Mechanical Properties of Single-Crystal Tantalum (100) Surface Covered with Anodic Oxide Film, *ibid.*

M. Seo, M. Hagioi; Changes in Mass and Stress during Anodic Oxidation and Cathodic Reduction of the Cu/Cu₂O Multilayer Film, International Symposium on "Progress in Corrosion Research" in Commemoration of Centenary of Birth of Professor Go Okamoto, Sapporo, Sep. 14-16, 2005. (Invited lecture)

D. Kawamata, M. Seo; Nano-indentation of the Passive Single-Crystal Ni Surface, The 52nd Annual Meeting of Jpn. Soc. Corrosion Eng., Sapporo, Sep. 14-16, 2005.

M. Seo, D. Kawamata; Nano-scratching in Solution to the Ta(100) Surface Subjected to Anodic Oxidation, The 56th Annual Meeting of the International Society of Electrochemistry, Busan, Korea, Sep. 25-30, 2005. (Invited lecture)

K. Fushimi, K. Azumi, M. Seo; Application of Short Voltage Pulse Polarization and Shear-force Sensing to Improve Resolution of SECM, *ibid.*

K. Azumi, T. Kurihara, K. Nishimura, M. Seo; Analysis of Initial Stage of Electroless Ni-P Plating on Al Alloys, *ibid.*

M. Nakajima, K. Azumi, M. Seo; Estimation of the Corrosion Rate of Titanium in Acid Solution, *ibid.*

A. Naganuma, K. Fushimi, K. Azumi, M. Seo; Fabrication of Micro-disk Electrode by Ni Electroless Plating, *ibid.*

K. Azumi, K. Iokibe, M. Seo; MO Simulation of Surface Diffusion of Zinc Adatoms on Zinc Surface, The 208th ECS meeting, Los Angeles, CA, USA, Oct. 16-21, 2005.

K. Fushimi, K. Takase, K. Azumi, M. Seo; Current Transients from Passive Iron Surface During Micro-Indentation, *ibid.*

M. Seo, T. Yamaya; Local Cathodic Corrosion of n-type InP (001) by Scratching, *ibid.*

Paper

Formation of Microparticles from Titanium and Silicon Electrodes Using High-Voltage Discharge in Electrolyte Solution

K. Azumi, A. Kanada, M. Kawaguchi, and M. Seo
J. Surf. Fin. Soc. Jpn. **56**, 938-941 (2005)

Small particles of Ti and Si were produced using a high-voltage discharge technique in aqueous solution. A Ti or Si electrode was cathodically polarized at a cell voltage higher than 180 V in an electrolyte solution to trigger spark discharge between the electrode surface and the electrolyte solution. The spark discharge generated intense heat at the spark point and emitted melted materials into solution. This process produced small particles of electrode materials in the solution. The particle size was in the range of ten nm to sub- μm for Ti and to 10 μm for Si. XRD spectra indicated that the surfaces of Ti particles were covered with oxide that had formed due to high-temperature oxidation in the aqueous solution. In the case of Si particles, XRD spectra showed only peaks attributed to Si crystal. (Japanese)

Cathodic reduction of the duplex oxide films formed on copper in air with high relative humidity at 60 °C

M. Seo, Y. Ishikawa, M. Kodaira, A. Sugimoto, S. Nakayama, M. Watanabe, S. Furuya, R. Minamitani, Y. Miyata, A. Nishikata and T. Notoyo
Corros. Sci., **47**, 2079-2090 (2005)

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 -2.5 mA cm^{-2} . The surface characterization 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 Cu₂O layer is reduced to metallic Cu. (English)

Simultaneous oscillation of specific surface energy, surface mass and electrode potential in the course of galvanostatic oxidation of formic acid

G. G. Lang, M. Seo and K. E. Heusler
J. Solid State Electrochem., **9**, 347-353 (2005)

Simultaneous oscillations of electrode potential, surface mass and specific surface energy have been detected in the course of galvanostatic oxidation of formic acid on platinum by using a Koesters laser interferometer combined with an electrochemical quartz crystal microbalance. Changes of surface energy data measured with the electrochemical Koesters laser interferometer and with the electrochemical bending beam technique are shown to be equivalent. Problems related to the interpretation of the measured data are discussed. (English)

Selective formation of porous layer on n-type InP by anodic

etching combined with scratching

M. Seo and T. Yamaya

Electrochim. Acta, **51**, 787-794 (2005)

The selective formation of porous layer on n-type InP (001) surface was investigated by using scratching with a diamond scribe followed by anodic etching in deaerated 0.5 M HCl. Since the InP specimen was highly doped, the anodic etching proceeded in the dark. The potentiodynamic polarization showed the anodic current shoulder in the potential region between 0.8 and 1.3 V (SHE) for the scratched area in addition to the anodic current peak at 1.7 V (SHE) for the intact area. The selective formation of porous layer on the scratched area was brought by the anodic etching at a constant potential between 1.0 and 1.2 V (SHE) for a certain time. The nucleation and growth of etch pits on intact area, however, took place when the time passed the critical value. The cross section of porous layer on the scratched area perpendicular to the $[\bar{1}10]$ or $[110]$ scratching direction had a V-shape, while the cross section of porous layer on the scratched area parallel to the $[\bar{1}10]$ or $[110]$ scratching direction had a band structure with stripes oriented to the $[\bar{1}11]$ or $[1\bar{1}1]$ direction. Moreover, nano-scratching at a constant normal force in the micro-Newton range followed by anodic etching showed the possibility for selective formation of porous wire with a nano-meter width. (English)

Hydrogen Evolution by Plasma Electrolysis in Aqueous Solution

T. Mizuno, T. Akimoto, K. Azumi, T. Ohmori, Y. Aoki and A. Takahashi

Jpn. Soc. Applied Physics, **44**, 396-401 (2005)

Hydrogen has recently attracted attention as a possible solution to environmental and energy problems. If hydrogen should be considered an energy storage medium rather than a natural resource. However, free hydrogen does not exist on earth. Many techniques for obtaining hydrogen have been proposed. It can be reformulated from conventional hydrocarbon fuels, or obtained directly from water by electrolysis or high-temperature pyrolysis with a heat source such as a nuclear reactor. However, the efficiencies of these methods are low. The direct heating of water to sufficiently high temperatures for sustaining pyrolysis is very difficult. Pyrolysis occurs when the temperature exceeds 4000°C. Thus plasma electrolysis may be a better

alternative, it is not only easier to achieve than direct heating, but also appears to produce more hydrogen than ordinary electrolysis, as predicted by Faraday's laws, which is indirect evidence that it produces very high temperatures. We also observed large amounts of free oxygen generated at the cathode, which is further evidence of direct decomposition, rather than electrolytic decomposition. To achieve the continuous generation of hydrogen with efficiencies exceeding Faraday efficiency, it is necessary to control the surface conditions of the electrode, plasma electrolysis temperature, current density and input voltage. The minimum input voltage required induce the plasma state depends on the density and temperature of the solution, it was estimated as 120 V in this study. The lowest electrolyte temperature at which plasma forms is -75°C . We have observed as much as 80 times more hydrogen generated by plasma electrolysis than by conventional electrolysis at 300 V. (English)

Hydrogen absorption monitoring of sputter-deposited Ti film in seawater

K. Azumi and M. Seo

Corros. Sci., **47**, 2470-2476 (2005)

Hydrogen absorption in Ti film sputter-deposited on glass plate immersed in sodium chloride solution of seawater concentration was monitored using resistometry. Increase in electric resistance due to increase in hydrogen content or growth of hydride in Ti during cathodic polarization was evaluated. A monitoring system was developed in which a couple of Ti films were used to reduce influence of temperature-fluctuation on resistance; one was used as a working electrode exposed to electrolyte solution and another was used as a reference resistance with silicon sealant coating. Two films were connected electrically in series, and applied by constant AC to measure resistance of the working electrode as relative value against the reference resistance. Increase in resistance during cathodic polarization at 0.8 V(RHE) was observed after some induction period. Scratching test during cathodic polarization did not provide major effect on hydrogen absorption. (English)

Nanoindentation and Nanoscratching Techniques for Evaluation of Mechanical Properties of Surface Films

Analytical Methods in Corrosion Science and Engineering, CRC Press, New York,

2005, p. 335- p. 360

Masahiro Seo

Nanoindentation and nanoscratching techniques have been recently developed to evaluate the mechanical properties of surface films such as hardness, elastic modulus and friction coefficient. In this chapter, the concrete procedures of these techniques were described and the mechanical properties of bulk oxides, anodic films and thin passive films evaluated by these techniques were discussed. Moreover, the attempts of nanoindentation and nanoscratching in solution for the specimen kept in passive state were introduced and the results obtained in solution were discussed from the mechano-electrochemical viewpoint. (English)

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

The topics of investigation are in the following:

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

Niobium covered with anodic oxide films were cathodically polarized in a neutral borate solution, and cyclic voltammetry (CV), electrochemical impedance

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

It was found from GDOES that hydrogen is enriched at the interface between oxide film and the metal substrate after a long cathodic polarization.

(2) Micro-patterning of anodic oxide films on aluminum by laser irradiation

Aluminum specimens covered with porous anodic oxide films were irradiated with a pulsed Nd-YAG laser by accurately controlling the laser energy and scanning rate. Only upper parts of the oxide film were found to be removed by laser irradiation, leading to the fabrication of micro-channels and micro-chambers on the oxide film.

(3) Initial stage of localized corrosion and corrosion protection with anodic oxide films on coated steels

Initial stage of localized corrosion in artificial pit formed on zinc and its alloy coated steels were examined by photon rupture method and also examined effect of anodic oxide film structure on corrosion protection of aluminum containing coated steels by polarization technique. An artificial micro pit can be formed in a coated layer by continuous focused pulsed YAG laser irradiation. The pit diameter remains constant and the depth increases with increasing time of irradiation. The pits formation speed in the coated layer is higher than that in the steel substrate. After laser irradiation, the rest potential changes in the negative direction while the zinc coated layer is exposed to the solution. However, after the steel substrate is also exposed to the solution, the rest potential changes in the positive direction. These differences in rest potential changes in direction can be explained by changes in the activated reactions by laser irradiation. The porous type anodic oxide films affect on corrosion protection of coated steels.

(4) Effect of anodic oxide film structure and thickness on corrosion protection of aluminum

Effect of anodic oxide film structure and thickness on corrosion protection of aluminum alloys were investigated by galvanic corrosion test and polarization measurements. The anodized 1100-H14 and 6061-T6 show good corrosion resistance from the results of galvanic corrosion tests and polarization measurements. Especially, composite type anodic oxide film specimens show the best corrosion resistance. The imperfections form in anodic oxide films during anodizing, and these were influence on corrosion resistance of anodized specimens. However the number and size of imperfections may be decrease with re-anodizing and this increases corrosion resistance.

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

Cylindrical Al-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 at laser-irradiated area. Then, acrylic acid resin was deposited on Au layer before dissolution of anodic oxide films and the metal substrate in NaOH solution. Finally, poly-pyrrole films were deposited on the back-side of the gold layer from pyrrole / sodium dodecyl-benzene sulfonate solutions. Acrylic acid resin / gold / poly-pyrrole three-layered cylindrical structure with four projections showed a gripping motion in solutions by repeating anodic / cathodic polarization.

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

Aluminum foils covered with thin barrier type anodic oxide films were set at the bottom of an electrochemical cell on the stage of atomic force microscope (AFM) and then solutions containing small particles of acrylic acid-/ melamine-resin were added in the cell. Under cathodic polarization in the solution, the specimen was scratched by a diamond probe of AFM and then anodically polarized. A dome-shaped acrylic acid-/ melamine-resin was deposited at the scratched area. The size of deposited resin increased with increasing anodic polarization time, scratched area, and compressive force of probe during scratching.

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

A photon rupture method, oxide film removed by focused pulsed Nd-YAG laser beam irradiation, applied to investigate localized repair of passive oxide films of titanium. The specimens were irradiated with a focused pulse of a pulsed Nd - YAG laser beam at a constant potential in $8.1 \text{ mol/m}^3 \text{ Na}_2\text{HPO}_4 / 5 \text{ mol/m}^3 \text{ KH}_2\text{PO}_4$ solutions with $140 \text{ mol/m}^3 \text{ NaCl} + 50 \text{ mol/m}^3 \text{ KCl}$ (PBS) at different potential and temperature, and the current transients were monitored. The current increases with increasing applied potential and chloride concentration. The oxide film, however, repair in every experimental conditions. The oxide film formation kinetics did not follow the inverse logarithmic law according to Cabrera-Mott theory. The peak current and current after laser irradiation increase with Cl^- concentration. The oxide film reformation time decreases with increasing Cl^- concentrations and solution temperature.

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

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

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

Aluminum specimens were coated with Nb_2O_5 films by a sol-gel electrophoretic method, and then anodized galvanostatically in a neutral boric acid / borate solution. Anodizing of Nb_2O_5 film-coated specimens lead to the formation of anodic oxide films consisting of an outer Al-Nb composite oxide layer and an inner alumina layer. Parallel capacitance of anodic oxide films obtained thus was appreciably larger than that obtained on specimens without any coating.

(11) Deterioration of anodized aluminum in iron para-toluenesulfonate solutions

Iron para-toluenesulfonate is used as oxidizing reagents in the deposition of poly-ethylenedioxythiophene(PEDT) on aluminum for manufacturing solid type electrolytic capacitors. Aluminum specimens covered with barrier type anodic oxide films were immersed in iron para-toluenesulfonate / buthanol solutions with different water contents to examine the deterioration of the anodized specimen. Imperfections in anodic oxide films became larger by the solution penetration during immersion, and eventually allowed the metal substrate to dissolve locally. Deterioration rate of the anodized specimen was higher at higher water contents, showing a maximum at 30–50 % of water contents. Beyond 50% of water contents, the deterioration rate became lower as water content became higher.

(12) Local electro-deposition on anodic oxide films with micro droplet cell

The flow type micro droplet cell was applied to form nickel line on copper and anodized aluminum. The nickel line and dots can form on copper substrate and the volume increases with increasing applied current. The width of nickel line does not change with cell moving speed, but the thickness depends on cell moving speed. Combine with photon rupture method, it is possible to form nickel line on anodized aluminum.

(13) Electrochemical Behavior of Welded Stainless Steels and AFM Observation of SCC

SCC cracks of welded stainless steel were observed by atomic force microscopy, AFM and electrochemical behavior at welded part studied by using flow type micro droplet cell. Microstructure difference between corrosion cracks and SCC cracks can be observed by AFM and SCC propagates splitting from the tip. The rest potential difference between steel substrate and welded metals can be measured with the flow type micro droplet cell. From these results SCC may initiate near welded parts, HAZ, due to the galvanic couple.

(14) Platinum coating on ceramics by electroless- and electro-plating

Thick platinum layers were formed on sintered ceramics by successive processes of electroless- and electro-plating. The ceramic specimens were immersed in HF solution, and then sensitizing and activating were carried out to deposit Pd

particles on the specimen. After activating, a thin layer of platinum could be deposited uniformly on the specimens by electroless-plating in $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2 / \text{N}_2\text{H}_4$ solution. The thin platinum coated specimens were immersed in a $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2 / \text{CH}_3\text{COONa} / \text{Na}_2\text{CO}_3$ solution, and then cathodically polarized to form thick platinum layer for 540 min. The platinum layer obtained thus was uniform and 70 μm thick.

Other activities

In June and July, Prof Takahashi and Assoc. Prof. Sakairi attended “Passivity 9” in Paris, and presented papers entitled “Oxide Films on Aluminum by Electrophoretic Sol - Gel Coating / Anodizing” (Takahashi) and “Initial stage of localized corrosion in artificial pit formed on zinc coated steels by photon rupture” (Sakairi). Takahashi visited Prof. P. Schmuki at Univ. of Erlangen – Nurnberg and gave a lecture on “Aluminum Surface Science and Technology Based on Anodizing” before “Passivity 9”. After the conference Sakairi visited, Dr. A. W. Hassel, Max Planck Inst. for Iron Research, Dusseldorf, Germany, Prof. Wolfgang Schuhmann, Universitt Bochum, Germany, and Prof. R. Schuster, Technische Universitt Darmstadt, Germany. At Max Planck Inst., he presented his resent study entitled "Initial stage of localized corrosion of metals in chloride ions containing solutions."

On 8th of August, Korea-Japan Mini-Symposium on the Development of New Types of Capacitors was held in Sapporo. Profs. W. Sugimoto, Y-S. Tak, H. Habazaki, S-G. Park, and H. Takahashi talked recent works on electrolytic and super capacitors. On the same day, Korea-Japan Mini-Symposium on Applied Electrochemistry of Students, by Students, and for Students was held, and 11 graduate students introduced their recent results.

In September, International Symposium for the Commemoration of One Centenary Anniversary of Go Okamoto's Birth was held in Sapporo, and LIMSA staff was involved in the organizing committee. Takahashi, Sakairi, and Nagahara attended the 56th Meeting of ISE held in Busan, Korea, in September, and presented papers entitled “Deposition of Organic Compounds at Selected Area on Aluminum by AFM Probe Processing and Electrochemical Technique” (Takahashi),” Fabrication of Three - Electrode Type Micro Electrochemical Cell by Photon Rupture - Effect of Solution Flow Rate” (Sakaiari), Electrochemical Noise Study on Galvanic Corrosion

of Anodized Aluminum Alloy in Chloride Environments” (Sakairi), “Initial Stage of Localized Corrosion in Artificial Pit Formed in Coated Steels by Photon Rupture” (Sakairi), and “Influence of Anodizing Condition on the Formation of Sunflower - like Imperfections in Anodic Oxide Films on Niobium” (Nagahara). During the ISE meeting, they visited Dr. Moon at KIMM in Changwon. Takahashi gave a lecture on “Laser and AFM Work on Aluminum at Hokkaido University”, and Sakairi presented the paper entitled "Initial Stage of Localized Corrosion of Metals by Photon Rupture Method".

In October, Sakairi and Kikuchi attended the 204th ECS meeting at Los Angeles, the symposium of "Corrosion and Electrochemistry of Advanced Materials in Honor of Koji Hashimoto", and they presented papers entitled on “Initial Stage of Localized Corrosion on Titanium in Phosphate Buffer Solution by Photon Rupture” (Sakairi), “Electrochemical Noise Study on Galvanic Corrosion of Aluminum Alloy in Chloride Environment - Effect of Oxide Film Structure –“ (Sakairi), and “Micromachining of Aluminum by Anodizing, Laser Irradiation, and Electrochemical Etching” (Kikuchi).

Foreign scientists visited LIMSA in 2005 were Prof. Y-S. Tag, Inha Univ. and Prof S-G. Park, Chungbuk Univ. on 7th – 10th of August, Prof. F. Di Quarto, Palermo Univ, Prof. R. Oltra, University of bourgogne on 14th – 18th of September, and Dr. S. C. Kwon on 1st – 3rd of December.

Presentations

Electrochemical Noise Analysis During Galvanic Corrosion of Aluminum; M. Sakairi, Y. Shimoyama and H. Takahashi : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, Jan., 2005.

Influence of Solution Temperature and Concentration on Structure and Dielectric Property of Anodic Oxide Films on Niobium; K. Nagahara, M. Sakairi, H. Takahashi, K. Takayama, and Y. Oda : The Hokkaido Secs. of Chem. Soc. Jpn. and Soc. Anal. Chem., Sapporo, Feb., 2005.

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

Formation of Anodic Oxide Films with High Potential Sustainability by Electrophoretic Sol-Gel Coating / Anodizing; M. Sunada, M. Sakairi, S. Hirai, K. Watanabe, and H. Takahashi : *ibid.*

Effect of Solution Flow Rate on Electrochemical Behavior of Aluminum Electrochemical Micro-reactor; Y. Yamada, M. Sakairi and H. Takahashi : The Joint Meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Feb., 2005.

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

Rest Potential Change During Continuous Laser Irradiation on Zn Alloy Coated Steels; Y. Uchida, M. Sakairi and H. Takahashi : *ibid.*

Local Deposition of Organic Compounds on Aluminum by Electrochemical AFM; S. Kurokawa, T. Kikuchi, M. Sakairi and H. Takahashi : *ibid.*

Development of Aluminum Surface Technology Based on Anodizing ; H. Takahashi : The 111th Annual Meeting of Surf. Finish. Soc. Jpn., Chiba, Mar., 2005.

Fabrication of 3D Platinum Microstructures by Laser Irradiation and Electrochemical Technique; T. Kikuchi, M. Sakairi, H. Takahashi, and T. Maruko : *ibid.*

Influence of Solution Temperature and Concentration on Structure and Dielectric Properties of Anodic Oxide Films on Niobium; K. Nagahara, M. Sakairi, H. Takahashi, K. Takayama, and Y. Oda : *ibid.*

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

Experimental study of two and three-dimensional superconducting network; S.

Tsuchiya, T. Kikuchi, H. Takahashi, K. Inagaki, and S. Tanda : International Conference on "Topology in Orderd Phases" (TOP2005), Sapporo, Mar., 2005.

Study on Initial Stage of Localized Corrosion on Coated Steels with Photon Rupture; Y. Uchida, M. Sakairi and H. Tahakashi : The 72th Annual Meeting of the Electrochem. Soc. of Jpn., Kumamoto, April, 2005.

Local Deposition of Acrylic Acid- / Melamine-Resin on Aluminum by Electrochemical AFM; S. Kurokawa, T. Kikuchi, M. Sakairi and H. Tahakashi : *ibid.*

Effect of Anodic Oxide Film Structure on Galvanic Corrosion of 6061 Al Alloy; Y. Shimoyama, M. Sakairi and H. Takahashi : Zairyo-to-Kankyo 2005, May, 2005.

Fabrication of Metal Electrochemical Micro-reactor by Photon Rupture Method; M. Sakairi, M. Yamada and H. Takahashi : The 66th Discussion Meeting of Jpn. Soc. Anal. Chem., Kitami, May, 2005.

Cathodic Polarization of Aluminum Covered with Anodic Oxide Films in a Neutral Solution; H. Takahashi : 32nd Meeting of Corrosion Evaluation Committee, Tokyo, May, 2005.

Fabrication of 3D PGM Microstructures by Laser Irradiation and Electrochemical Technique; T. Kikuchi : Lilac Seminar, Ootaki, June, 2005.

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BIOMEDICAL, DENTAL MATERIALS AND ENGINEERING LABORATORY

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The research activities cover (1)the development, evaluation and application of dental and biomedical materials, (2)the development of methods and equipments for fabrication of materials and prostheses and (3)the measurement of properties. These are concerned with mechanical, thermal properties, corrosion, surface treatment, biocompatibility, bioreactivity, estheticity and various methods of imaging and microanalyses. Many researches are related to dental, biological and engineering fields and performed in collaboration with clinical departments including Removable Prosthetic Dentistry(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 μ m and 10 μ m Ti particles suggests that

the particles(1-3 μ m) smaller than cell size(about 5 μ m in neutrophils) induces cytotoxicity as a result of phagocytosis, while for particles larger than cell size(10 μ m) phagocytosis is not possible, resulting in the less clear cytotoxicity effect.

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

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

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

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

Laser lithography, one of the CAD/CAM systems to fabricate the polymer models by piling up the thin slices, which are photo-polymerized by scanning laser beam originally on the shallow depth of liquid epoxy monomer, was applied for the fabrication of dental 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 Co^{60} and electrons on one of the main matrix polymer UDMA(urethane dimethacrylate) for dental composite resin were investigated with various mechanical tests and spectroscopies. C^{+} ion radiation induced the large change in the structure sensitive properties of mechanical properties, Vickers hardness, flexural strength, abrasion resistance and little change in the non-structure sensitive properties of spectroscopies, FT-IR, Raman scattering, Fluorescence, NMR and thermal expansion coefficient. The results suggest that the mechanism of radiation effect is mostly due to the physical structure change such as lattice defects of vacancies, interstitials, depleted zone rather than the chemical effect of cross-linking by further progress of 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 μ m thickness is coherent to matrix Ti and is strong enough. Abraded volume by ultrasonic scaler was increased with the load on Ti, while no trace was formed on Ti(-N), instead the stainless tip of scaler was abraded. The test showed that abrasion would be negligibly small under the practical conditions of the load 50g in clinics. Ti(-N) with biocompatibility and surface abrasion resistance would be suitable as abrasion-resistant implant materials for the application to the artificial joint of implant and abutment part of dental implant.

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

The current photocatalysis of anatase TiO₂ mostly works only by ultraviolet light. To make it applicable for medical use it is necessary to develop 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" finish for the three year as Research on Advanced Medical Technology under Health and Laybour Sciences Research Grants from the Ministry of Health, Laybour and Welfare of Japan. The project team is constitute of Leader: Prof.Fumio WATARI, Assigned Researchers: 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.

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.

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, University Polytechnica Bucharest, Bucharest, Romania (Dr. ROSCA Iosif Daniel) on the development of polymer biomaterials.

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

Presentations

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Surface carbide formation on titanium for abrasion resistant implant material YH. Zhu, M. Shimozuma, M. Uo, W. Wang, T. Akasaka, F. Watari, The 5th Asian BioCeramics Symposium, Sapporo, Jan, Oct, 2005.

Size separation of carbon nanotubes for biomedical applications, K. Tohji, Y. Sato, A. Yokoyama, K. Shibata, S. Ogino, K. Tamura, T. Akasaka, M. Uo, K. Motomiya, B. Jeyadevan, R. Hatakeyama, F. Watari, International Symposium on EcoTopia Science, Nagoya, Aug, 2005.

Water-soluble hat-stacked carbon nanofibers for biomedical applications, Y. Sato, K. Shibata, F. Bunshi, A. Yokoyama, S. Ogino, K. Tamura, T. Akasaka, M. Uo, K. Motomiya, B. Jeyadevan, R. Hatakeyama, F. Watari, K. Tohji, International

Symposium on EcoTopia Science, Nagoya, Aug, 2005.

Biochemical and Pathological response of human macrophage to micro/nano particles, K. Tamura, N. Takashi, M. Uo, T. Akasaka, Y. Totsuka, F. Watari, International Symposium on EcoTopia Science, Nagoya, Aug, 2005.

A local structure of Ni impurity in Carbon nanotube studied by XAFS and multiple scattering analysis, K.Asakura, W-J.Chun, M.Ushiro, K.Uno, T.Fujikawa, Y.Sato, K.Tohji, F.Watari, International Symposium on EcoTopia Science, Nagoya, Aug, 2005.

Tissue Response to Carbon Nanosubstances: Comparison between Carbon Nanotubes and Hat-Stacked Carbon Nanofibers by Transmission Electron Microscopy, A.Yokoyama, Y.Sato, Y.Nodasaka, S.Yamamoto, N.Aoki, M.Shindoh, T.Kohgo, T.Akasaka, M.Uo, K.Tohji, F.Watari, International Symposium on EcoTopia Science, Nagoya, Aug, 2005.

Fabrication and properties of sintered carbon nanotubes, W.Wang, A. Yokoyama, M. Omori, S. Liao, T. Akasaka, M. Uo, F. Watari, , International Symposium on EcoTopia Science, Nagoya, Aug, 2005.

Microparticles of biodegradable polymers, I.D. Rosca, F.Watari, P.O.Stanescu, Romanian International Conference on Chemistry and Chemical Engineering, Bucharest, Sep., 2005.

Homogenous dispersions of multiwalled carbon nanotubes in aqueous phase, I.D. Rosca, F.Watari, P.O.Stanescu, Romanian International Conference on Chemistry and Chemical Engineering, Bucharest, Sep., 2005.

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

LABORATORY OF ADVANCED MATERIALS CHEMISTRY

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H. Onishi, T. Kasashima, M. Kiri

The research activities of the laboratory are directed toward (1) formation, characterization and properties of nanocarbons, carbon-based composites and carbides, (2) tailoring of novel materials for electrolytic capacitor, electrochemical capacitor and lithium ion battery, (3) formation of anodic oxide on valve metals and their alloys with functional properties and (4) biological minewater treatment utilizing carbon fibers.

Current research topics are in the following:

- (1) Preparation of carbon nanocarbons 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. We have prepared successfully carbon nanofilaments and brush-type nanocarbons by liquid phase carbonization of

polymers in the templates. Superior high rate capability of the carbon nanofilaments as anode materials for lithium ion batteries has been found.

(2) Anode characteristics of Si-C-O glassy materials for lithium ion batteries

Si-C-O glassy materials prepared from silicone and exfoliated graphite or urethane form at elevated temperatures were examined to be used for anodes of lithium ion batteries. The materials formed at selected conditions revealed very high charge-discharge capacity in addition to good cycle performance. Only a problem for practical application is a large irreversible capacity at the first cycle. Various treatments has been carried out to reduce the irreversible capacity.

(3) Manganese oxide – carbon hybrid materials for electrochemical capacitors

Manganese dioxide is one of promising electrodes for electrochemical capacitors, but its low electronic conductivity is a drawback for the application. Manganese dioxide has been deposited on to exfoliated graphite by various chemical treatments, and electrochemical capacitor properties of the obtained hybrid materials of carbon and manganese dioxide have been investigated.

(4) Influence of carbon fibers on biological treatment of wastewater containing manganese ions

Removal of manganese(II) ions from manganese-rich minewater using a manganese-oxidizing fungus under the presence of carbon fibers has been examined. Carbon fibers accelerate effectively the oxidation of manganese ions. Various carbon materials and fibrous materials other than carbon have been added in the minewater containing the fungus. It has been found that carbon fibers are most effective in accelerating the oxidation. No influence of other fibrous materials has been seen. The performance of the deposited porous manganese oxide for electrochemical capacitors has also been investigated.

(5) Field crystallization of anodic niobia

Various factors influencing field crystallization of amorphous anodic niobia, which is a potential candidate dielectrics of tantalum electrolytic capacitor, has been examined. The mechanism of the field crystallization is proposed, based on the results obtained. Significant importance of foreign species incorporated from electrolyte and substrate, as well as modification of the structure of an air-formed oxide formed before anodizing has been clarified to suppress the field crystallization.

(6) Spark anodizing 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.

(7) Formation of porous anodic oxides in hot glycerol electrolyte containing phosphate

Porous anodic alumina films are formed in a new electrolyte of water-free hot glycerol containing phosphate ions. Influences of phosphate concentration, acidity and basicity of the electrolyte, formation voltage and anodizing time on morphology and thickness of the oxide films.

Other activities

In July, Dr. Wan, coming from China, joined our laboratory as a postdoctoral fellow. Mr. Tauseef, from Pakistan, entered Graduate School of Engineering, Hokkaido University.

Professor Konno attended International Conference on Carbon in 2005 (CARBON 2005) held at Gyeongju, Korea in July. Associate Professor Habazaki attended the 9th International Symposium on Passivation of Metals and Semiconductors and the Properties of Thin Oxide Layers held at Paris, France in

June and the 56th Annual Meeting of the International Society of Electrochemistry held at Busan, Korea in September. Professor Konno and Associate Professor Habazaki attended the 208th ECS Fall Meeting held at Los Angeles, USA in October. Associate Professor was one of organizers of the Symposium on Corrosion and Electrochemistry of Advanced Materials; in Honor of Koji Hashimoto, held in this Meeting.

Presentations

Preparation of TiC/Fe composites using exfoliated graphite: D. Abe, H. Habazaki, H. Konno: The Winter Joint Meeting of Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., Sapporo, Feb., 2005.

Anode characteristics of Si-C-O glass composites for lithium ion batteries: S. Sato, H. Habazaki, H. Konno, T. Morishita, M. Inagaki: The joint Meeting of Hokkaido Secs. of ECSJ, SFSJ and JSCE, Sapporo, Feb. 2005.

Electrochemical properties of MnO₂/exfoliated graphite for pseudo-electrochemical capacitors: Y. Takahashi, H. Habazaki, H. Konno: The joint Meeting of Hokkaido Secs. of ECSJ, SFSJ and JSCE, Sapporo, Feb. 2005.

Electrochemical decomposition of phenol using carbon electrodes: A. Nowaki, H. Habazaki, H. Konno, The joint Meeting of Hokkaido Secs. of ECSJ, SFSJ and JSCE, Sapporo, Feb. 2005.

Mechanism of crystallization of anodic niobia: T. Ogasawara, H. Habazaki, H. Konno, K. Shimizu, S. Nagata, K. Takayama, K. Oda: The joint Meeting of Hokkaido Secs. of ECSJ, SFSJ and JSCE, Sapporo, Feb. 2005.

Synthesis of nano-carbon materials by liquid phase carbonization in porous templates: M. Hayashi, H. Habazaki, H. Konno, M. Inagaki: The joint Meeting of Hokkaido Secs. of ECSJ, SFSJ and JSCE, Sapporo, Feb. 2005.

Formation mechanism of crystalline anodic niobia: T. Ogasawara, H. Habazaki, H. Konno, K. Shimizu, S. Nagata, K. Takayama, K. Oda: 111th Meeting of SFSJ, Chiba, Mar., 2005.

Application of low voltage-high resolution BSE imaging to nano-surface analysis: K. Shimizu, S. Tachibana, H. Habazaki: 111th Meeting of SFSJ, Chiba, Mar., 2005.

Analysis and observation of electrodeposited hard gold films using rf-GDOES, low voltage FE-SEM/ESB and cross-sectional TEM: K. Shimizu, S. Tachibana, H. Habazaki: 111th Meeting of SFSJ, Chiba, Mar., 2005.

Preparation of porous templates by anodizing of DC etched Al foils and their application to synthesis of nanocarbons: M. Hayashi, H. Habazaki, H. Konno, M. Inagaki: 111th Meeting of SFSJ, Chiba, Mar., 2005.

Analysis of various surface films formed on aluminium by rf-GDOES: K. Shimizu, H. Habazaki: 111th Meeting of SFSJ, Chiba, Mar., 2005.

Anode characteristics of Si-C-O films coated on graphite flakes for lithium ion batteries: H. Konno, T. Morishita, S. Sato, H. Habazaki, M. Inagaki: 72th Meeting of the Electrochemical Society of Japan, Kumamoto, Apr., 2005.

Structure and dielectric properties of zirconium anodic oxide films: H. Habazaki, H. Konno, K. Shimizu, K. Asami, S. Nagata: 72th Meeting of the Electrochemical Society of Japan, Kumamoto, Apr., 2005.

Influence of oxygen in substrate on thermal stability of anodic niobium oxide: H. Habazaki, T. Ogasawara, H. Konno, K. Shimizu, K. Asami, S. Nagata, K. Takayama, Y. Oda: 72th Meeting of the Electrochemical Society of Japan, Kumamoto, Apr., 2005.

Synthesis of porous SiC from silicone and its properties: S. Sato, H. Habazaki, H. Konno: 72th Meeting of the Electrochemical Society of Japan, Kumamoto, Apr., 2005.

Structural change of carbon nanofilaments prepared from porous alumina template with heat treatment temperature: M. Hayashi, H. Habazaki, H. Konno, M. Inagaki, 273th Meeting of 117 JSPS committee for Carbon Materials, Tokyo, Apr., 2005.

Formation of barrier- and porous-type anodic oxide films on valve metals: H. Habazaki, K. Shimizu: 73th ARS Meeting, Tokyo, Apr., 2005.

Amorphous Si-C-O compounds/exfoliated graphite composites for negative electrode materials of lithium ion battery: H. Konno, T. Morishita, S. Sato, H. Habazaki, and M. Inagaki: Carbon2005, Gyeongju, Korea, Jul., 2005.

Formation and characterization of carbon micro-spheres containing boron and nitrogen: H. Konno, R. Matsuura, A. Sudoh, and H. Habazaki: Carbon2005, Gyeongju, Korea, Jul., 2005.

Spark anodizing of β -Ti alloy for improvement of wear resistance: T. Onodera, H. Habazaki, H. Konno, H. Takazawa, K. Toyotake, H. Kashiwase: The Summer Meeting of Hokkaido Secs. of Chem. Soc. Jpn., Hakodate, Jul., 2005.

Factors influencing field crystallization of anodic niobia: T. Ogasawara, H. Habazaki, H. Konno, S. Nagata, K. Takayama, Y. Oda: The Summer Meeting of Hokkaido Secs. of Chem. Soc. Jpn., Hakodate, Jul., 2005.

Oxidative removal of Mn(II) ions from minewater using various fungus: Y. Ogawa, K. Sasaki, K. Takano, H. Konno, H. Habazaki: The Summer Meeting of Hokkaido Secs. of Chem. Soc. Jpn., Hakodate, Jul., 2005.

Structure and electrochemical properties of carbon nanofilaments prepared using porous anodic alumina templates, H. Habazaki, M. Hayashi, M. Kiri, K. Konno and M. Inagaki, The 56th Annual Meeting of International Society of Electrochemistry, Busan, Sep., 2005.

Observation of cross-sections of electroless-plated plastics using low voltage

FE-SEM/ESB: K. Shimizu, S. Tachibana, Y. Kasahara, H. Habazaki: 112th Meeting of SFSJ, Kanazawa, Oct., 2005.

Factors influencing growth of crystalline anodic niobia: T. Ogasawara, H. Habazaki, H. Konno, K. Shimizu, S. Nagata: 112th Meeting of SFSJ, Kanazawa, Oct., 2005.

Formation of hard coating on β -Ti alloy by spark anodizing: T. Onodera, H. Habazaki, H. Konno, H. Takazawa, K. Toyotake, H. Kashiwase: 112th Meeting of SFSJ, Kanazawa, Oct., 2005.

Preparation of Si-C-O glass-like compounds using urethane form template for anode of lithium ion batteries: H. Konno, T. Morishita, S. Sato, H. Habazaki, M. Inagaki: 112th Meeting of SFSJ, Kanazawa, Oct., 2005.

Field crystallization of anodic niobia on Nb-O substrates, H. Habazaki, T. Ogasawara, H. Konno, K. Shimizu, K. Asami, S. Nagata, K. Takayama, P. Skeldon, G. E. Thompson, 208th Meeting of the Electrochemical Society, Los Angeles, Oct. 2005.

Si-C-O glass-like compounds as a negative electrode material for Li ion battery, H. Konno, T. Morishita, S. Sato, H. Habazaki, M. Inagaki, 208th Meeting of the Electrochemical Society, Los Angeles, Oct. 2005.

Preparation of nano-carbons using templates formed by anodizing of etched Al foils: 22th ARS conference, Aomori, Nov. 2005.

Synthesis of boron carbide micro-crystals from hydrothermally prepared sugar-boric acid composites: A. Sudo, H. Habazaki, H. Konno: 32nd Ann. Meeting of the Carbon Soc. of Jpn., Ueda, Dec., 2005.

Li ion insertion/extraction characteristics of Si-C-O glass-like compounds: H. Konno, T. Morishita, S. Sato, H. Habazaki, M. Inagaki: 32nd Ann. Meeting of the Carbon Soc. of Jpn., Ueda, Dec., 2005.

Li ion insertion/extraction characteristics of carbon nanofilaments formed by the liquid-phase carbonization using templates: M. Kiriū, M. Hayashi, H. Habazaki, H. Konno: 32nd Ann. Meeting of the Carbon Soc. of Jpn., Ueda, Dec., 2005.

Comparison of the promoting effect of carbon materials on the removal of Mn(II) ions from drainage by fungus: Y. Ogawa, H. Tachibana, H. Konno, K. Sasaki: 32nd Ann. Meeting of the Carbon Soc. of Jpn., Ueda, Dec., 2005.

Facilities and Capabilities

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

X-ray diffractometer: Rigaku RINT2000, capable of θ -2 θ and α -2 θ 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 an argon 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.

Charge-discharge instrument for batteries: Hokuto HJ-SM8, capable of 8 channel measurements

LABORATORY OF HIGH TEMPERATURE MATERIALS

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Research work at “Laboratory of high temperature materials” directs toward 1) high temperature oxidation of metals and intermetallics, 2) evaporation behavior of metal oxides in H₂O-containing atmospheres, 3) interface reactions between metals and silicides, 4) sintering and synthesis of silicide-based composites, and 5) silicide coating on metals.

Current topics on research are in the following:

(1) Silicide coatings on carbon steel

High temperature performance (reaction at silicide/steel interface and oxidation resistance) of silicide (NiSi₂ and CrSi₂) coatings deposited on a carbon steel by air plasma spraying is being investigated. These results on the high temperature performance demonstrated that the proposed coating system is proof against severe oxidizing atmospheres containing sulfur, chlorine below 1073 K.

(2) Oxidation behavior of metal disilicides.

In order to clarify the oxidation behavior of metal disilicides, high-temperature oxidation tests are being done. In particular, the requisite vapor pressure of metal oxide for the formation of a SiO_2 scale was clarified from the observation of the oxide scales formed on W and Cr disilicides.

(3) Effect of B-addition on oxidation of metal disilicides

The effect of B-addition on oxidation of CrSi_2 and WSi_2 are being investigated. The results demonstrated that the addition of B was very effective for the improvement of the oxidation resistance of the metal disilicides. In addition, microstructure and oxidation resistance of new Mo-Si-B composites are being investigated.

(4) Microstructure of oxide scales formed on NiAl-X alloys

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

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

In order to clarify the effect of H_2O vapor on oxidation behavior of steels in a hot rolling process, oxidation tests of some carbon steels at 1473 K in $(\text{N}_2\text{-}3\%\text{O}_2)\text{-XH}_2\text{O}$ atmospheres are being done. The results showed that the position of spalling of oxide scale during cooling moved to from the substrate/oxide scale interface to the $(\text{Fe}_3\text{O}_4+\text{FeO})/\text{FeO}$ interface with increase in oxidation temperature and time.

(6) High temperature oxidation of aluminum alloys

In order to clarify the oxidation mechanism of aluminum alloys, oxidation tests of them are being carried out in air and H_2O -containing atmospheres. In particular, relationship between formation of nodule-like oxides and alloying elements is being investigated.

Other activities:

Dr. Akira Yamauchi joined this laboratory as a post-doctoral fellow in January. His work in this laboratory is “Development of new silicide-based composites having high oxidation resistance”. In September, Ms. Yamada joined this laboratory as a research assistant.

In September, Prof. Kurokawa attended the Fifth International Symposium on Applied Plasma Science held in Kona, Hawaii, U. S. A. as one of organizers, and also presented a paper entitled “Oxidation behavior of Plasma Sprayed Ni-Si Coatings on the Carbon Steel Substrate”. In July, Dr. Yamauchi attended the International Symposium on Metastable and Nano Materials held in Paris, France, and presented a paper entitled “Synthesis of Mo-Si-B *In-situ* Composites by Mechanical Alloying”. After the symposium he visited Max-Planck-Institute in Düsseldorf. In November, Prof. Kurokawa and Dr. Yamauchi attended the International Symposium on High-Temperature Oxidation and Corrosion 2005 held in Nara, Japan, and presented two papers entitled “Microstructures of SiO₂ scales formed on MoSi₂” and “TDS measurement of hydrogen released from stainless steel oxidized in H₂O-containing atmospheres”.

Presentations

High Temperature Properties of CrSi₂ Coatings on Carbon Steel; S. Tsubouchi and K. Kurokawa: The 12th Annual Meeting of Inst. of Applied Plasma Sci., Toyohashi, Mar., 2005.

Spalling and Structures of Oxide Scales Formed on Steel in Atmospheres Simulated Heating Condition Prior to Hot Rolling; K. Kurokawa and S. Nishizawa: Meeting of The Research Group on Oxide Scale on Steel, Iron and Steel Inst. Jpn., Osaka, Jan., 2005.

Evaporation Behavior of Cr_2O_3 and Degradation of Cr_2O_3 Scale in H_2O -Containing Atmospheres; A. Yamauchi and K. Kurokawa: 2005 Symposium on Materials & Systems for Energy Conversion, Sapporo, Mar., 2005.

Characteristic of Al_2O_3 Scale Formed on NiAl Alloys; S. Kawata, A. Yamauchi, K. Kurokawa, S. Watanabe, and T. Narita: *ibid.*

Nano-structural Analyses of The Oxide Scale/Substrate Interfaces Formed in NiAl Alloy; S. Watanabe, S. Kawata, A. Yamauchi, K. Kurokawa and T. Narita: *ibid.*

Effect of B Addition on Oxidation Behavior of CrSi_2 in H_2O -Containing Atmospheres; N. Takada and K. Kurokawa, The 137th Annual Meeting of Jpn. Inst. Metals, Yokohama, Mar., 2005.

Preparation and Oxidation Resistance of CrSi_2 -Ni; S. Tsubouchi and K. Kurokawa: *ibid.*

Effect of Aging on Surface Oxidation of Single Crystal FeAl; A. Yamauchi, M. Tsunekane, K. Yoshimi, H. Takanashi, and S. Hanada, *ibid.*

Preparation of Mo-Si-B Composites by Mechanical Alloying and Their Phase Transformation; A. Yamauchi, K. Kurokawa, K. Yoshimi, and S. Hanada, *ibid.*

Effect of Scale Structure on Surface Properties of Steel; K. Kurokawa: Meeting of The Section of Hot-Rolling Process, Iron and Steel Inst. Jpn., Kure, July, 2005.

Synthesis of Mo-Si-B *In-situ* Composites by Mechanical Alloying; A. Yamauchi, K. Yoshimi, K. Kurokawa, and S. Hanada: The International Symposium on Metastable and Nano Materials, Paris, France, July, 2005.

Growth Behavior and Structure of Al_2O_3 Scale Formed on NiAl; S. Kawada, A. Yamauchi, S. Watanabe, K. Kurokawa, and T. Narita: The Summer Joint

Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July., 2005.

Oxidation behavior of Plasma Sprayed Ni-Si Coatings on the Carbon Steel Substrate; Y. N. Wu, Y. Kawahara, and K. Kurokawa: The Fifth International Symposium on Applied Plasma Science, Hawaii, U. S. A., Sep., 2005.

Structure of Al_2O_3 Scale Formed on NiAl; S. Kawada, A. Yamauchi, S. Watanabe, K. Kurokawa, T. Narita: The 138th Annual Meeting of Jpn. Inst. Metals, Hiroshima, Sep., 2005.

Oxidation Behavior of CrSi_2 -Ni Composites; S. Tsubouchi, A. Yamauchi, K. Kurokawa, and Y. Kawahara: *ibid.*

Synthesis Process of Mo-Si-B In-Situ Composites by Powder Metallurgy; A. Yamauchi, K. Kurokawa, and K. Yoshimi: *ibid.*

High-Temperature Corrosion Resistance and Applying for Sprayed Coating of CrSi_2 ; S. Tsubouchi, K. Kurokawa, A. Yamauchi, and Y. Kawahara: The 52th Jpn. Conf. on Materials and Environments, Sapporo, Sep., 2005.

Effect of Alloying Elements on Structure of Oxide Scale Formed on NiAl-X Alloy; K. Kurokawa, S. Kawada, A. Yamauchi, S. Watanabe, and T. Narita: Annual Meeting of 123 Committee of Jpn. Soc. Promotion of Sci., Tokyo, Nov., 2005.

Microstructures of SiO_2 Scales Formed on MoSi_2 ; K. Kurokawa, D. Goto, J. Kuchino, A. Yamauchi, T. Shibayama, and H. Takahashi: International Symposium on High-Temperature Oxidation and Corrosion 2005, Nara, Japan, Nov.-Dec., 2005.

TDS Measurement of Hydrogen Released from Stainless Steel Oxidized in H_2O -Containing Atmospheres; A. Yamauchi, Y. Yamauchi, Y. Hirohata, T. Hino and K. Kurokawa: *ibid.*

Facilities and Capabilities

Spark Plasma Sintering Equipment

Ultra-High Vacuum Furnace with Mass Spectrometer

Oxidation Test Equipment with Thermobalance and Ultra-High Temperature Furnace

Optical Microscope with High Temperature Furnace

Laboratory of Advanced High Temperature Materials

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Yamazaki,
T. Akagiri, M. Sakata, Y. Kitajima, J. Aoyama, J. Sato, T. Sekimoto, and S.
Tonouchi

The research activities of the laboratory are directed to an understanding of the mechanism of the high temperature corrosion and oxidation of metals such as superalloys, intermetallic compounds, iron-based heat resistant alloys. Development of the corrosion/oxidation resistant coating for the protection of

high temperature alloys is one of the most important research activities in our research project.

Current topics on research are in the following:

- (1) Development of multiphase diffusion barrier coating on TiAl intermetallic compounds
- (2) Development of Re-Cr based diffusion barrier coating on Ni-based superalloys
- (3) Effect of Pt on the oxidation of Ni-based alloys
- (4) Effect of fourth elements on the oxidation behavior of Fe-Cr-Al based alloys.

Presentations

Development of an Oxidation Resistant Coating on Ultra-High Temperature Nb-based Alloy; T. Narita, K. Saito, S. Hayashi, M. Sohma, I. Iwanaga, K. Fjita, Y. Matsumura and R. Tanaka : Jpn, Inst. Metals, March 2005

Oxidation Behavior of γ -Ni-Al-Pt Alloys; S. Hyashi, T. Narita and B. Gleeson : Jpn, Inst. Metals, March 2005

Growth of reaction layer on Cu plate dipped into Sn-Ag and Sn-Ag-Cu Pb-free solders; S. Saito, H. Ohsima, T. Narita, J. Tanaka and T. Takashima : Jpn, Inst. Metals, March 2005

Oxidation behavior of the Oxidation Resistant Coatings on TiAl Alloy in air containing water vapor; T. Nishimoto, T. Izumi, S.Hayashi and T.Natita : Jpn, Inst. Metals, March 2005

Formation of Re-based Diffusion Barrier Coating on Nb-based Alloy; K. Saito, S.Hayashi and T.Natita : Jpn, Inst. Metals, March 2005

Interdiffusion Behavior of Ni-based Superalloy / σ -Re-Ni-Cr (W) alloy / Ni-Al alloys; H. Matsumaru, S.Hayashi and T.Natita : Jpn, Inst. Metals, March 2005

Effect of third elements on the oxidation behavior of Ni₃Al Alloys; S. Mikuni, S.Hayashi and T.Natita : Jpn, Inst. Metals, March 2005

Relationship between microstructure and thermal fatigue properties of Sn-low In-Al Pb-free solder for metal/ceramics board joining; H. Mizuno, J. Tanaka and T.Narita : Jpn, Inst. Metals, March 2005

Mechanical Properties of Oxidation Resistant Coating on Ni based Superalloy; M. Sakata, S.Hayashi and T.Natita : Jpn, Inst. Metals, March 2005

Phase Equilibria of the Ni-Al-Cr Systems at 1423K and 1173K; Y. Kitajima, S.Hayashi and T.Natita : Jpn, Inst. Metals, March 2005

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Interdiffusion between Ni based superalloy and diffusion barrier coatings at 1423K; H. Matsumaru, S.Hayashi and T.Natita: International Symposium on High-temperature Oxidation and Corrosion, Nara, Japan, Nov., 2005

Influence of a third element on the high temperature oxidation behavior of the γ' -Ni₃Al alloys; S. Mikuni, S.Hayashi and T.Natita: International Symposium on High-temperature Oxidation and Corrosion, Nara, Japan, Nov., 2005

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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

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Characterization of Rust Layer on Weathering Steel

T. Ohtsuka

The 36th Seminar on Corrosion Engineering – Engineering System for Weathering Steel, JSCE (2005), p.37

Characterization of the rust layers on weathering steels exposed in various site for 17 or 18 years was done by 6 laboratories.

The weight loss of the weathering steel and thickness of the rust layer on the steel increases with air-borne salt in environment of the exposure site. The rust layer formed in the environment containing air-borne salt with high concentration includes β - and δ - FeOOH. The AC conductivity measured under wet condition depends on the air-borne salt concentration, increasing with the concentration. The diffusion coefficient of water vapor through the rust layer and specific surface area of the rust measured by N₂ adsorption are correlated with the concentration. (Japanese)

Molecular Assembly of Manganese Mesoporphyrin Derivatives on a Gold Electrode and Their Electron Transfer Activity

T. Yamada, S. Kikushima, T. Hikita, S. Yabuki, M. Nagata, R. Umemura, M. Kondo, T. Ohtsuka and M. Nango

Thin Solid Films, **474**, 310-321 (2005)

Disulfide-linked manganese mesoporphyrin derivatives with spacer methylene-chain groups (C_n), $(MnMP-C_n-S)_2$ [$n=2, 6, 12$] and one fluorinated mesoporphyrin derivative, $(MnMPF_4-C_{12}-S)_2$ (Scheme 1) were synthesized and assembled on a gold electrode to study the nature of their electron transfer with respect to catalytic activity. The electron transfer of the mesoporphyrins from and to the self-assembled monolayers (SAMs) was measured in aqueous solution as well as in dimethyl sulfoxide (DMSO) using cyclic voltammetry and potential modulation reflectance, i.e., electroreflectance. Redox reaction of the mesoporphyrins on the electrode occurred between Mn(III) and Mn(II) occluded in the porphyrin ring. The rate constants of the electron transfer from and to the manganese mesoporphyrins on gold electrodes, estimated from the ER vs. modulation frequency relation, increased with the decreasing chain lengths but decreased due to fluorination of the porphyrin ring, which is in agreement with the rates for tetraphenyl porphyrins and its halogenated derivatives. Interestingly, the rate constants for the manganese mesoporphyrins in DMSO were greater than the rates for the tetraphenyl porphyrins and were enhanced by additional insertion of alkanethiols into the SAMs in aqueous solution.

Behavior of Silver Electrode in $\text{AlCl}_3\text{-NaCl-AgCl}$ Melt

T. Sato, M. Ueda and I. Saeki

Electrochemistry, **73**, 736-738(2005)

Limiting current densities of silver deposition in $\text{AlCl}_3\text{-NaCl-AgCl}$ or LiCl-KCl-AgCl melts, and change in the equilibrium potential of silver with AlCl_3 concentration were measured to consider a large potential difference in the two melts. Diffusion rate of silver species in $\text{AlCl}_3\text{-NaCl-AgCl}$ melt was concluded to be much slower than that in LiCl-KCl-AgCl melt. The formation of a silver complex in $\text{AlCl}_3\text{-NaCl-AgCl}$ melt was suggested. The equation, $\text{Ag} + \text{AlCl}_4^- = \text{AgAlCl}_4 + e^-$ or $\text{Ag} + 2\text{AlCl}_4^- = \text{Ag}(\text{AlCl}_4)_2^- + e^-$, might be a possible electrochemical reaction of silver in the melt.

Electrodeposition of Al-Cr-Ni Layer by Pulse Electrolysis in AlCl_3 -EMIC Molten Salt

M. Ueda, H. Ebe and T. Ohtsuka

Electrochemistry, **73**, 739-741(2005)

To improve the oxidation resistance of TiAl intermetallic compounds under high temperature conditions, electrodeposition of an Al, Cr, and Ni layer was carried out by constant potential control or potential pulse control in AlCl_3 -EMIC (1-ethyl-3-methyl-imidazolium chloride) ambient-temperature molten salt containing NiCl_2 and CrCl_2 at 338K. The electrodeposition of Al, Cr, and Ni occurred at potentials lower than 0.0V vs. Al/Al^{3+} . Ni concentration in the deposit was about 9 at% at 0 V. However, it decreased with a decrease in potential to 1 at% at -0.2V . The potential pulse technique enhanced the Ni concentration in the deposit to 20-27 at%. Cr Concentration was also enhanced by pulse potential control: the concentration of Cr was raised to 15 at%. In all electrodeposits, sharp peaks corresponding to Al metal were detected with a relatively high background by XRD analysis. It is conceivable that deposit layers consisting of Al, Cr, and Ni may be amorphous.

Enhancement of Electric Conductivity of the Rust Layer by Adsorption of Water

T. Ohtsuka and T. Komatsu

Corrosion Science, **47**, 2571-2577 (2005)

The rust layers on the weathering steels exposed for 17 or 18 y at seven different sites in Japan were studied by electrochemical impedance under wet condition and measurement of amount of water vapor adsorbed. The transient of amount of adsorbed water vapor into the rust layer during humidity jump from 0% to 80% RH indicated that saturation of adsorbed water vapor took place within 1 h. From the semi-infinite model of diffusion, apparent diffusion coefficients of H₂O in the rust were calculated. It was found the apparent diffusion coefficient was higher when the amount of air-borne salt of exposure sites was higher. The impedance diagram of the rusted steels was analyzed with an equivalent circuit consisting of a series connection between an ohmic resistance and a parallel circuit of charge transfer resistance-redox capacitance. The double layer capacitance on the gold electrodes pressed onto the rust layer was further added on the circuit. The impedance showed that the rust layer behaved as a dielectric layer under dry condition, while the conductance was greatly enhanced with wet condition. The charge transfer resistance evaluated from the simulation under wet condition was largely dependent on the amount of air-borne salt in environment. It was concluded that the rust layer formed in the site with relatively large amount of air-borne salt revealed high conductivity under wet condition. For the rust formation followed by the Evans model during wet-dry cycles, the higher conductivity induced the more facilitative reduction of the rust layer under wet condition and the larger growth of the rust layer in a wet-dry cycle.

Recovery of Aluminum from Oxide Particles in Aluminum Dross Using AlF_3 – NaF – BaCl_2 Molten Salt

M. Ueda, S. Tsukamoto, S. Konda and T. Ohtsuka

Journal of Applied Electrochemistry, **35**, 925-930 (2005)

To recover aluminum from aluminum dross, a floating separation of aluminum alloy from the oxides and subsequent electrolysis of the oxides was carried out in a molten salt bath of 33 mol% AlF_3 , 51 mol% NaF and 16 mol% BaCl_2 . With A356.0 casting alloy dross, 83% of the aluminum alloy was recovered by the floating separation. A further 4% of metallic aluminum was recovered by electrolysis in the molten salt containing the oxides separated from the dross. The optimum current for continuous operation is discussed considering a balance between the electrowinning and dissolution rates.

Availability of Synchrotron Radiation for Corrosion Engineering

T. Ohtsuka

The 151st Symposium of Corrosion and Corrosion Protection –Application of Synchrotron Radiation to Corrosion Science and Engineering, JSCE (2005), p.19

Availability of Synchrotron Radiation X-ray technique was reviewed. For the passive oxide film, in-situ X-ray technique should be applied to examine the hydration-dehydration process in the film. The process may be related to the electric field through the film. For the rust layer on weathering steel, the reactions should be examined under wet-dry condition, where the rust undergoes reduction accompanied by oxidation of the substrate steel under wet condition and reoxidation of the rust takes place under the following dry condition. (Japanese)

Formation of Microparticles from Titanium and Silicon Electrodes Using High-Voltage Discharge in Electrolyte Solution

K. Azumi, A. Kanada, M. Kawaguchi, and M. Seo

J. Surf. Fin. Soc. Jpn. **56**, 938-941 (2005)

Small particles of Ti and Si were produced using a high-voltage discharge technique in aqueous solution. A Ti or Si electrode was cathodically polarized at a cell voltage higher than 180 V in an electrolyte solution to trigger spark discharge between the electrode surface and the electrolyte solution. The spark discharge generated intense heat at the spark point and emitted melted materials into solution. This process produced small particles of electrode materials in the solution. The particle size was in the range of ten nm to sub- μm for Ti and to 10 μm for Si. XRD spectra indicated that the surfaces of Ti particles were covered with oxide that had formed due to high-temperature oxidation in the aqueous solution. In the case of Si particles, XRD spectra showed only peaks attributed to Si crystal. (Japanese)

Cathodic reduction of the duplex oxide films formed on copper in air with high relative humidity at 60 °C

M. Seo, Y. Ishikawa, M. Kodaira, A. Sugimoto, S. Nakayama, M. Watanabe, S. Furuya, R. Minamitani, Y. Miyata, A. Nishikata and T. Notoya

Corros. Sci., **47**, 2079-2090 (2005)

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 -2.5 mA cm^{-2} . The surface characterization 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 Cu₂O layer is reduced to metallic Cu. (English)

Simultaneous oscillation of specific surface energy, surface mass and electrode potential in the course of galvanostatic oxidation of formic acid

G. G. Lang, M. Seo and K. E. Heusler

J. Solid State Electrochem., **9**, 347-353 (2005)

Simultaneous oscillations of electrode potential, surface mass and specific surface energy have been detected in the course of galvanostatic oxidation of formic acid on platinum by using a Koesters laser interferometer combined with an electrochemical quartz crystal microbalance. Changes of surface energy data measured with the electrochemical Koesters laser interferometer and with the electrochemical bending beam technique are shown to be equivalent. Problems related to the interpretation of the measured data are discussed. (English)

Selective formation of porous layer on n-type InP by anodic etching combined with scratching

M. Seo and T. Yamaya

Electrochim. Acta, **51**, 787-794 (2005)

The selective formation of porous layer on n-type InP (001) surface was investigated by using scratching with a diamond scribe followed by anodic etching in deaerated 0.5 M HCl. Since the InP specimen was highly doped, the anodic etching proceeded in the dark. The potentiodynamic polarization showed the anodic current shoulder in the potential region between 0.8 and 1.3 V (SHE) for the scratched area in addition to the anodic current peak at 1.7 V (SHE) for the intact area. The selective formation of porous layer on the scratched area was brought by the anodic etching at a constant potential between 1.0 and 1.2 V (SHE) for a certain time. The nucleation and growth of etch pits on intact area, however, took place when the time passed the critical value. The cross section of porous layer on the scratched area perpendicular to the $[\bar{1}10]$ or $[110]$ scratching direction had a V-shape, while the cross section of porous layer on the scratched area parallel to the $[\bar{1}10]$ or $[110]$ scratching direction had a band structure with stripes oriented to the $[\bar{1}11]$ or $[1\bar{1}1]$ direction. Moreover, nano-scratching at a constant normal force in the micro-Newton range followed by anodic etching showed the possibility for selective formation of porous wire with a nano-meter width. (English)

Hydrogen Evolution by Plasma Electrolysis in Aqueous Solution

T. Mizuno, T. Akimoto, K. Azumi, T. Ohmori, Y. Aoki and A. Takahashi

Jpn. Soc. Applied Physics, **44**, 396-401 (2005)

Hydrogen has recently attracted attention as a possible solution to environmental and energy problems. If hydrogen should be considered an energy storage medium rather than a natural resource. However, free hydrogen does not exist on earth. Many techniques for obtaining hydrogen have been proposed. It can be reformulated from conventional hydrocarbon fuels, or obtained directly from water by electrolysis or high-temperature pyrolysis with a heat source such as a nuclear reactor. However, the efficiencies of these methods are low. The direct heating of water to sufficiently high temperatures for sustaining pyrolysis is very difficult. Pyrolysis occurs when the temperature exceeds 4000°C. Thus plasma electrolysis may be a better alternative, it is not only easier to achieve than direct heating, but also appears to produce more hydrogen than ordinary electrolysis, as predicted by Faraday's laws, which is indirect evidence that it produces very high temperatures. We also observed large amounts of free oxygen generated at the cathode, which is further evidence of direct decomposition, rather than electrolytic decomposition. To achieve the continuous generation of hydrogen with efficiencies exceeding Faraday efficiency, it is necessary to control the surface conditions of the electrode, plasma electrolysis temperature, current density and input voltage. The minimum input voltage required induce the plasma state depends on the density and temperature of the solution, it was estimated as 120 V in this study. The lowest electrolyte temperature at which plasma forms is -75°C. We have observed as much as 80 times more hydrogen generated by plasma electrolysis than by conventional electrolysis at 300 V. (English)

Hydrogen absorption monitoring of sputter-deposited Ti film in seawater

K. Azumi and M. Seo

Corros. Sci., **47**, 2470-2476 (2005)

Hydrogen absorption in Ti film sputter-deposited on glass plate immersed in sodium chloride solution of seawater concentration was monitored using resistometry. Increase in electric resistance due to increase in hydrogen content or growth of hydride in Ti during cathodic polarization was evaluated. A monitoring system was developed in which a couple of Ti films were used to reduce influence of temperature-fluctuation on resistance; one was used as a working electrode exposed to electrolyte solution and another was used as a reference resistance with silicon sealant coating. Two films were connected electrically in series, and applied by constant AC to measure resistance of the working electrode as relative value against the reference resistance. Increase in resistance during cathodic polarization at 0.8 V(RHE) was observed after some induction period. Scratching test during cathodic polarization did not provide major effect on hydrogen absorption. (English)

Nanoindentation and Nanoscratching Techniques for Evaluation of Mechanical Properties of Surface Films

Analytical Methods in Corrosion Science and Engineering, CRC Press, New York, 2005, p. 335- p. 360

Masahiro Seo

Nanoindentation and nanoscratching techniques have been recently developed to evaluate the mechanical properties of surface films such as hardness, elastic modulus and friction coefficient. In this chapter, the concrete procedures of these techniques were described and the mechanical properties of bulk oxides, anodic films and thin passive films evaluated by these techniques were discussed. Moreover, the attempts of nanoindentation and nanoscratching in solution for the specimen kept in passive state were introduced and the results obtained in solution were discussed from the mechano-electrochemical viewpoint. (English)

Anodic Film Growth on Al Layers and Ta-Al Metal Bilayers In Citric Acid Electrolytes

A. Mozalev, I. Mozalev, M. Sakairi, and H. Takahashi

Electrochim. Acta, **50**, 5065-5075 (2005)

A systematic investigation has been undertaken of anodising behaviour of aluminium in citric acid solutions under changing the current density, electrolyte temperature, concentration and stirring conditions. Porous films of steady-state, controlled and extraordinary large morphologies have been obtained at the formation voltages of 260–450 V. The barrier layer thickness, cell and pore diameters appeared to be directly proportional to the formation voltage. For the first time, a porous anodic film with cell diameter of 1.1 μm , barrier layer thickness of 0.5 μm and pore diameter of 0.23 μm was naturally grown on aluminium in 0.125 mol dm⁻³ citric acid electrolyte. The selected electrical and electrolytic conditions have been applied to sputter-deposited Ta–Al bilayers. The tantalum underlayer was anodised through the initially grown at 450 V porous alumina film with the formation of tantalum oxide ‘columns’ penetrating into the pores and mixing with the outer part of the alumina cell walls. During subsequent constant current reanodising of the Ta–Al bilayers in 0.5 mol dm⁻³ H₃BO₃, the voltage rose up to 1100 V, until voltage fluctuations terminated normal oxide growth. The columns thickened uniformly up to 1.42 μm with the nmV⁻¹ ratio of 1.3, exhibiting nearly ideal dielectric behaviour up to almost 1000 V of the formation voltage. The outer column material is composed mainly of stoichiometric Ta₂O₅ mixed with small amount of Al₂O₃, while the innermost column material is tantalum monoxide with little content of boron species. Implications of these findings for the formation of composite dielectrics for high-voltage electrolytic capacitors are discussed.

Local Breakdown of Anodic Oxide Films on Aluminum Contacting with Solid Electrolytes

M. Yamada, M. Sakairi, H. Takahashi, K. Nogami, and H. Uchi

ECS Proc. Volume 2002-24, 66-77 (2005)

Aluminum specimens were coated with anodic oxide films by anodizing in a neutral borate solution after either electropolishing or sol-gel coating, and then attached to an organic conductive polymer, poly-ethylenedioxythiophene (PEDT) and aluminum counter electrode. Impedance and film breakdown measurements were carried out for the specimen attached to PEDT, to compare their Characteristics with those obtained for the specimen without PEDT in a neutral solution. Parallel capacitance, C_p , obtained for the specimen with PEDT decreased with increasing film formation potential, E_f , and was smaller than that obtained for the specimen without PEDT. The decrease in C_p by attachment of PEDT was considered to be due to the decrease in the effective area at the interfaces between anodic oxide film / PEDT and between PEDT / Al counter electrode. Film breakdown voltage, V_b , of the specimen with PEDT was proportional to E_f , for oxide films formed at $E_f < 100$ V, and remained almost constant at $V_b = 100$ V above $E_f > 100$ V. The behavior of film breakdown was very similar on both electropolished and SiO_2 -coated specimens. Film breakdown mechanism is discussed in terms of the chemical bond breaking and the electron injection from PEDT.

Analysis of the Initial Stage of Localized Corrosion on Zn and Zn Alloy Coated Steels by Photon Rupture Method

Masatoshi SAKAIRI, Kazuma ITABASHI and Hideaki TAKAHASHI

ISIJ Int., **45**, 71-76 (2005)

A photon rupture method, film removal by a focused pulse of pulsed Nd- YAG laser beam irradiation, has been developed as it enables oxide film stripping at extremely high rates without contamination from the film removal tools. In the present study, Zn and Zn - 5 mass% Al alloy coated steel specimens covered with protective nitrocellulose film were irradiated with a focused pulse of a pulsed Nd - YAG laser beam at a constant potential in $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_3$ - $0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$ (pH = 7.4) with / without 0.05 kmol m^{-3} of chloride ions to investigate the initial stage of localized corrosion. At low potentials, both samples reformed oxide film after the nitrocellulose films were removed by this method. The oxide film formation kinetics of Zn - 55 mass % Al follow an inverse logarithmic law, in agreement with Cabrera-Mott theory. However, at high potentials, localized corrosion producing corrosion products occurred at the area where nitrocellulose film was removed. The dissolution current of the Zn coated steel samples is higher than that of Zn - 5 mass % Al coated samples at the same applied potential.

The Initial Stage of Pitting Corrosion on Coated Steels Investigated by Photon Rupture in Chloride Containing Solutions

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

Corrosion Sci., **47**, 2461-2469 (2005)

A photon rupture method, film removal by a focused pulse of pulsed Nd- YAG laser beam irradiation, has been developed to enable oxide film stripping at extremely high rates without contamination from the film removal tools. In the present study, Zn - 55 mass% Al alloy and Al - 9 mass % Si alloy coated steel specimens covered with protective nitrocellulose film were irradiated with a focused pulse of a pulsed Nd - YAG laser beam at a constant potential in $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_3$ - $0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$ (pH = 7.4) with 0.01 kmol m^{-3} of chloride ions to investigate the initial stage of localized corrosion. At low potentials, both coated alloys reformed oxide film after the nitrocellulose films were removed by this method. The oxide film formation kinetics follow an inverse logarithmic law, in agreement with Cabrera-Mott theory. However, at high potentials, localized corrosion producing corrosion products occur at the area where nitrocellulose film was removed. Nevertheless when the applied potential is less noble, the dissolution current of the Zn - 55 mass% Al coated steel samples is higher than that of Al - 9 mass % Si coated samples.

Effect of Anions on Initial Stage of Localized Corrosion of Zn- 55 mass% Al Alloy Coated Steels by Photon Rupture Method and Anodizing

Masatoshi Sakairi, Kazuma Itabashi and Hideaki Takahashi

Zairyo-to-Kankyo, **54**, 494-500 (2005)

Photon rupture with a focused single pulse of pulsed YAG-laser irradiation was used to investigate abrupt destruction and repair of passive oxide films or localized corrosion on anodized Zn - 55 mass% Al coated steels. The specimens were irradiated with a focused pulse of a pulsed Nd - YAG laser beam at a constant potential in borate solutions, pH = 9.2, with and without Cl^- , NO_3^- , and SO_4^{2-} ions and the current transients were monitored. The oxide films were reformed in the borate solution with NO_3^- and SO_4^{2-} ions after removal of the oxide film. The oxide film formation kinetics follows the inverse logarithmic law, according to Cabrera-Mott theory at the late stage after $t = 10$ ms. As the potential becomes nobler, the current increases. These behaviors can be explained by a preferential dissolution of the metal substrate, which is enhanced at nobler potentials and with the anions. In Cl^- containing solutions, localized corrosion of the coated layer occurs at high potentials, while film reformation occurs at low potentials.

Electrochemical Noise Study on Galvanic Corrosion of Anodized Aluminum in Chloride Environments

SAKAIRI Masatoshi, SHIMOYAMA Ukiya and TAKAHASHI Hideaki

ECS Proc. Volume 2004-14, 265-272 (2005)

Aluminum and aluminum alloys are usually used after surface treatment, namely anodizing which formed a barrier type or a porous type oxide film. The effect of the anodic oxide film structure on galvanic corrosion of aluminum was examined by electrochemical noise analysis technique in chloride ion containing solutions. As the thickness of both types of anodic oxide film increased, the incubation period of localized corrosion became longer. The power spectrum density of potential and impedance of electrochemical noise decreased with immersion time. The impedance of porous type anodic oxide films was larger than that of barrier type anodic oxide film.

Study on Initial Stage of Localized Corrosion on Coated Steels by Photon Rupture Method

M. Sakairi

J. Jpn. Soc. Colour Mater., 78 72-77 (2005)

A photon rupture method has been developed as it enables oxide film stripping at extremely high rates without contamination from the film removal tools. In the present paper explain the mechanism of film removal by this technique and also show the results of initial stage of localized corrosion of Zn alloy coated steel specimens in $0.5 \text{ kmol m}^{-3} \text{ H}_3\text{BO}_3$ - $0.05 \text{ kmol m}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$ (pH = 7.4) with / without 0.05 kmol m^{-3} of chloride ions by this technique. (Japanese)

Observation of microstructure of bulk specimens by ultra-microtomy, TEM and AFM

M. Sakairi

J. Surf. Fin. Soc. Jpn., **56**, 626 – 630 (2005)

This paper is an over view of how to use ultra microtomy using diamond knife to prepare thin specimens for transmission electron microscopy, TEM and atomic force microscopy. In this paper, cross sectional observation of anodized aluminum, niobium and etched pits formed in aluminum were shown. (Japanese)

Micromachining of Aluminum Surface by Laser Irradiation and Electrochemical Etching

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

J. Surf. Fin. Soc. Jpn., **56**, 409 – 414 (2005)

Microgrooves were fabricated on aluminum surface using anodizing, laser irradiation, and electrochemical etching. Aluminum specimen covered with porous type oxide films was irradiated with a pulsed Nd-YAG laser in distilled water to remove the anodic oxide film. The electrochemical etching of laser irradiated specimen in NaCl solution caused the formation of grooves with rough surface, while the electrochemical etching in $\text{CH}_3\text{COOH} / \text{HClO}_4$ solution caused the formation of grooves with flat surface. The width and depth of the grooves increased with electrochemical etching time. Mesh-like micro-pattern with a $70\mu\text{m}$ line width and $30\mu\text{m}$ line depth was fabricated on aluminum surface by consecutive processes of anodizing, laser irradiation, and electrochemical etching. (Japanese)

Fabrication of Micro-Circuit Board by Aluminum Anodizing and Laser Irradiation - Effect of Laser Irradiation Condition on Micro-Pattern Formation -

T. Kikuchi and H. Takahashi

J. Surf. Fin. Soc. Jpn., **56**, 528 – 534 (2005)

A prototype circuit board with micro-metal pattern was fabricated by laser irradiation and electrochemical technique. Aluminum specimen covered with porous type oxide films was irradiated with a pulsed laser beam, using convex lens with 10mm focal length. The oxide film was removed in irregularly shaped area, using 1.5mm diameter of laser beam, while the oxide film was removed in a circle with 5 μ m diameter, using 1.0mm diameter of laser beam, due to aberration of convex lens. Diameter of the film removed area decreased with decreasing laser power and laser irradiation time. Laser irradiation with a beam expander and a doublet lens caused the removal of the oxide film in a circle with 3 μ m diameter. Fine metal pattern of 4 μ m line width was fabricated on the epoxy resin board by successive steps of aluminum anodizing, laser irradiation, electroplating, resin attaching, and removal of aluminum substrate and oxide film. (Japanese)

***In situ* quantitative analysis of etching process of human teeth by atomic force microscopy**

F. Watari

J. Electron Microscopy, 54, 299-308 (2005)

Etching is one of the most fundamental steps in the restoration of teeth by adhesion of composite resin in dental clinics. Atomic force microscope (AFM) was used for the *in situ* observation of the etching process of human enamel, dentin and synthetic hydroxyapatite in the three different acid agents, 2% phosphoric acid, 10% citric acid and 10% polyacrylic acid. To measure the absolute depth from the initial level before etching and to correlate the surface height between the changing AFM images obtained, the depth profiles were recorded with etching time by carrying out the line scan consecutively at the representative place of the observed area. These chronological series of depth profiles enabled us to perform quantitative analysis of etched amount in addition to the surface roughness obtained from relative depth profile within one image. The course of etching process from the dissolution of smear layer, appearance of enamel prisms or dentinal tubules to progress of demineralization could clearly be observed. The depth profile, surface roughness, etching amount, etching rate and smear layer thickness could then be evaluated. The different etching characteristics of three acid agents and the effect of surface roughness produced by different mechanical prepolish were compared and discussed.

Rare earth oxide containing fluorescent glass filler for composite resin

M. Uo, M. Okamoto, F. Watari, K. Tani, M. Morita, A. Shintani

Dental Materials Journal, 24, 49-52 (2005)

In recent dental care, esthetic restorative materials such as composite resin and porcelains have been widely used and studied. However, their good esthetics makes the visual inspection of restored teeth difficult. In this study, a fluorescent glass filler containing rare earth oxides, which are well-known fluorescent materials, was prepared and used in composite resin to add visual inspection ability with small change in color. The Eu_2O_3 containing filler provided clear and visible fluorescence with irradiation by near ultraviolet light. The fluorescence intensity of the prepared composite resin was increased with the increase of the Eu_2O_3 content in the glass filler and the filler/resin ratio in the composite resin. The effect of the addition of Eu_2O_3 up to 10wt% to the glass filler on the color of the composite resin was quite small. Tb_4O_7 - and Dy_2O_3 -added fillers also showed clear fluorescence as Eu_2O_3 -added filler. Therefore, fluorescent glass fillers for composite resins were successfully prepared with small change in color.

Analysis of Titanium Dental Implants Surrounding Soft Tissue Using X-ray Absorption Fine Structure (XAFS)

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

Chemistry Letters, **34**, 776-777 (2005)

X-ray absorption fine structure (XAFS) analysis was applied for the analysis of titanium (Ti) in the human oral mucosa in contact with Ti dental implants from two different patients. Metallic Ti and an oxide (anatase) were detected. The metallic Ti was distributed in particulate form, which would be debris formed by the abrasion during the operation of implantation. The possibility of using XAFS for the analysis of the chemical state of rarely contained elements in biological tissue was suggested.

Nano-architecture on Carbon Nanotube Surface by Biomimetic Coating

T. Akasaka and F. Watari

Chemistry Letters, **34**, 826-827 (2005)

Calcium phosphate (Ca-P) coating on carbon nanotubes (CNTs) was done with a biomimetic coating method. The multi-walled CNTs (MWNTs) were immersed for 2 weeks in the simulated body fluid. Observation by scanning electron microscopy showed needle shape of Ca-P crystallites at nano-scale levels were massively grown on MWNTs. Thus the nano-architecture of crystalline Ca-P on MWNT surface could be produced by simple method and the MWNT may be acting as core for initial crystallization.

Biological Behavior of Hat-Stacked Carbon Nanofibers in the Subcutaneous Tissue in Rats

A. Yokoyama, Y. Sato, Y. Nodasaka, S. Yamamoto, T. Kawasaki, M. Shindoh, T. Kohgo, T. Akasaka, M. Uo, F. Watari and K. Tohji

Nanoletters, 1, 157-161 (2005)

The tissue response to hat-stacked carbon nanofibers (H-CNFs) was evaluated. H-CNFs were implanted in the subcutaneous tissue of rats. Histological and ultrastructural investigations were carried out by transmission electron microscopy. Although many macrophages and foreign body giant cells were seen around H-CNFs, no severe inflammatory response such as necrosis was observed. Some H-CNFs were observed in lysosomal vacuoles of phagocytes. These results showed that H-CNFs were not strong proinflammatory substances and were engulfed *in vivo*.

Oxidation of multiwalled carbon nanotubes by nitric acid

I.D. Rosca, F. Watari, M. Uo and T. Akasaka

Carbon, 42, 3124-3131 (2005)

The oxidation of MWCNTs in nitric acid was monitored using sample weight, Raman spectrum, solubility, morphology and alignment. The influence of the acid concentration, temperature and oxidation duration on the monitored parameters was assessed. A new method, based on optical microscopy is proposed for the determination of MWCNT solubility in concentrated aqueous suspensions. The investigations revealed that the solubility is determined not only by the functional groups on the MWCNT, but also by the functionalized amorphous carbon generated during the digestion of the nanotubes. High solubility (20–40 mg/ml) is obtained only after prolonged exposure (24–48 h) in concentrated acid (P60%). But in these conditions 60–90% of the MWCNTs are lost. Furthermore the MWCNTs are strongly fragmented and covered by amorphous carbon after 48 h of oxidation. It was found that the solubility correlates well with the area ratio of the G and D bands from the Raman spectrum. SEM examination of the MWCNT films showed extended alignment after 24 h of oxidation.

Cell Culture on a Carbon Nanotube Scaffold

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

Journal of Biomedical Nanotechnology, 1, 402-405 (2005)

The developments of nanoscale substance such as carbon nanotubes (CNTs) for medical applications have attracted a great deal of attention. In the present study, an attempt was made to development of CNTs as scaffolds for cell culture. CNT scaffolds were formed on polycarbonate membranes by vacuum filtration and cell proliferation and morphology were investigated using a scanning electron microscopy. Osteoblast cells (bone-forming cell) on CNTs showed excellent proliferation with extension of cell morphology in all directions. Numerous filopodia were extended from cells toward the inside of fibrous aggregates of CNTs and tightly bound to scaffolds. These results suggest that CNTs can be used as scaffolds with excellent affinity for cell adhesion.

A three-layered nano-carbonated hydroxyapatite/collagen/PLGA composite membrane for guided tissue regeneration

S. Liao, W. Wang, M. Uo, S. Ohkawa, T. Akasaka, K. Tamura, F. Cui and F. Watari

Biomaterials, 26, 7564-7571 (2005)

Functional graded materials (FGM) provided us one new concept for guided tissue regeneration (GTR) membrane design with graded component and graded structure where one face of the membrane is porous thereby allowing cell growth thereon and the opposite face of the membrane is smooth, thereby inhibiting cell adhesion in periodontal therapy. The goal of the present study was to develop a three-layered graded membrane, with one face of 8% nano-carbonated hydroxyapatite/collagen/poly(lactic-co-glycolic acid) (nCHAC/PLGA) porous membrane, the opposite face of pure PLGA non-porous membrane, the middle layer of 4% nCHAC/PLGA as the transition through layer-by-layer casting method. Then the three layers were combined well with each other with flexibility and enough high mechanical strength as membrane because the three layers all contained PLGA polymer that can be easily used for practical medical application. This high biocompatibility and osteoconductivity of this biodegraded composite membrane was enhanced by the nCHAC addition, for the same component and nano-level crystal size with natural bone tissue. The osteoblastic MC3T3-E1 cells were cultured on the three-layered composite membrane, the primary result shows the positive response compared with pure PLGA membrane.

Formation and Characterization of Carbon Micro-Spheres Doped with Boron and Nitrogen

H. Konno, R. Matsuura, K. Hajime; A. Sudoh, H. Habazaki, M. Inagaki

Tanso, **219**, 221-225 (2005)

Carbon micro-spheres doped with boron and nitrogen have been made from a chelate resin, in which N-methyl glucamate functional groups form ester with borate ions. Carbon spheres formed by heating at 1000-1600°C for 1 h in argon were 140-340 μm in diameter and the central ca. 1/3 of sphere was hollow. They contained 4.4-4.8 mass % of boron, and B/C and N/C mole ratios of the sphere surface increased markedly with raising heat treatment temperature. Most of boron and nitrogen atoms in the surface layer of 1600°C product were in the form of >B-N< bonds. Hardness and elastic modulus including Poisson's ratio were highest for the spheres produced at 1000°C, 1.24 GPa and 18.9 GPa, respectively, and decreased with raising HTT. Generally, oxidation resistance of spheres in pure oxygen increased with raising HTT, which may be owing to the increased amounts of surface >B-N< bonds.

Direct Loading of Fine Particles of Pd on Activated Carbon from Acidic Aqueous Solution and its NO Conversion Ability

T. Okuni, Y. Sahashi, A. Satsuma, H. Konno, M. Inagaki

Tanso, **217**, 95-98 (2005)

Direct loading of fine particles of metallic Pd on an activated carbon was found in an acidic solution of PdCl₂ at room temperature. Pd-loaded activated carbons thus prepared showed almost 100 % conversion of NO at a temperature above 350°C. The amount of Pd loaded on activated carbon could be controlled by the concentration of PdCl₂ in the solution.

The Valence State of Copper in Anodic Films Formed on Al-1at.% Cu Alloy

X. Zhou, G. E. Thompson, P. Skeldon, K. Shimizu, H. Habazaki and G. C. Wood

Corrosion Science, **47**, 1299-1306 (2005)

During anodising of Al-Cu alloys, copper species are incorporated into the anodic alumina film, where they migrate outward faster than Al^{3+} ions. In the present study of an Al-1at.% Cu alloy, the valence state of the incorporated copper species was investigated by X-ray photoelectron spectroscopy, revealing the presence of Cu^{2+} ions within the amorphous alumina film. However, extended X-ray irradiation led to reduction of units of CuO to Cu_2O , probably due mainly to interactions with electrons from the X-ray window of the instrument and photoelectrons from the specimen. The XPS analysis employed films formed on thin sputtering-deposited alloy/electropolished aluminium specimens. Such an approach enables sufficient concentrations of copper species to be developed in the anodic film for their ready detection.

A Tracer Study of Oxide Growth During Spark Anodizing of Aluminum

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

Journal of the Electrochemical Society, **152**, C382-C387 (2005)

Sequential anodizing is employed to investigate the mechanism of coating growth on aluminum under sparking in a phosphate electrolyte. Thus, coatings are formed in a silicate electrolyte and then in the phosphate electrolyte, with the location of phosphorus in the final coating being identified by electron probe microanalysis. The presence of silicon primarily in the outer region of the coating and of phosphorus primarily in the inner region of the coating indicates short-circuit transport of phosphorus species through the coating, with new coating material being formed in the vicinity of the metal/coating interface. The transport path is presumed to be associated with pores, cracks, and channels in the coating produced by dielectric breakdown events.

Nanoporous Anodic Niobium Oxide Formed in Phosphate/Glycerol Electrolyte

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

Electrochemical and Solid-State Letters, **8**, B17-B20 (2005)

High-resolution transmission electron microscopy and electron energy loss spectroscopy/energy-dispersive X-ray analysis were employed to reveal the development of nanoporous, amorphous anodic oxide films on niobium. The oxide was formed at 10 A m^{-2} in a dehydrated phosphate/glycerol electrolyte at 453 K. The relatively nonuniform pore network comprised pores about 5 nm wide, which connect the film surface to an similar to 5 nm thick barrier layer at the film base. The film is presumed to grow at the metal/oxide interface by inward migration of O^{2-} ions through the barrier layer, while field-assisted dissolution proceeds at the pore bases.

Oxidation-Resistant Multilayer Coatings Using an Anodic Alumina Layer as a Diffusion Barrier on γ -TiAl Substrates

T. Kuranishi, H. Habazaki and H. Konno

Surface & Coatings Technology, **200**, 2438-2444 (2005)

Diffusion barrier layers of anodic alumina, introduced between an oxidation-resistant Al-Nb-Cr alloy and γ -TiAl substrate, have been evaluated using scanning electron microscopy and electron probe microanalysis. Diffusion of titanium to the Al-Nb-Cr coating is obvious when the Al-Nb-Cr alloy coated directly on the TiAl substrate is oxidized at 900°C for 168 h. The anodic alumina layer has been introduced by sputter-depositing aluminum and subsequent anodizing of the aluminum layer at a constant current density in 0.01 mol dm⁻³ ammonium pentaborate electrolyte at 298 K. Then, the Al-Nb-Cr alloy is further sputter-deposited on the anodized specimens. It is clearly demonstrated that the thin anodic alumina layer, less than 500 nm thick, suppresses effectively the inter-diffusion between the oxidation-resistant alloy coating and the TiAl substrate, particularly when a thin aluminum layer is remained beneath the anodic alumina. Although microcracks are generated and the substrate is oxidized through the cracked regions for the coatings that contain the metallic aluminum layer, the oxidation of the substrate through the cracks is prevented by pre-oxidation treatment at 800°C.

High-Capacity Negative Electrode Materials Composed of Si-C-O Glass-Like Compounds and Exfoliated Graphite for Lithium Ion Battery

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

Carbon, **43**, 1111-1114 (2005)

Si-C-O glass like compounds/exfoliated graphite composites, containing 25 mass% O, showed large steady capacity as a negative electrode for lithium ion batteries. The title material composites were first synthesized as oxidation resistant graphite composites. Two types of silicone compounds, a cyclic type and a chain type having Si-H bonds, and a trace amount of Pt catalyst were impregnated into exfoliated graphite by sorption and dried at 50°C overnight, followed by curing in air at 200°C for 1 h. Graphite sheets were coated with a very thin silicone layer by this process. The composites were fabricated to negative electrodes and used in a glass cell with positive electrode and reference electrode both of Li foil. Charge discharge characteristics were measured in 1 mol/L LiClO₄ solution of EC/DEC (50/50 vol%).

Formation of Oxidation Resistant Graphite Flakes by Ultrathin Silicone Coating

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

Surface & Coatings Technology, **194**, 24-30 (2005)

Two types of silicone compounds and a trace amount of Pt catalyst were impregnated into exfoliated graphite (EG) by sorption and cured under different conditions. By this process, graphite sheets composing EG were coated with very thin ($\ll 1 \mu\text{m}$) silicone layer. Thus, obtained precursors were converted to oxidation resistant graphite flakes by the heat-treatment at a temperature in a range of 1000- 1300°C for 1 h in inert atmosphere. The coatings were intact and they were mixtures of Si-C-O glass-like composites and amorphous silica, which were confirmed by SEM, XRD and MAS-NMR. As formed graphite flakes showed instantaneous mass losses of 5-13% by oxidation at 1000°C for 1 h in pure O₂, but after that the mass change was very small. By removing free carbons on the surface beforehand, the mass loss became less than 1% for all products. The mass loss of the sample molded into a disk-shape was about 1% after the first cycle (1 h) of repetitive oxidation at 1000°C in air but from the second cycle an appreciable mass loss was not observed up to 20 h. The present method is promising for the production of oxidation resistant graphite flakes.

Influence of Film Composition on the Structure and Dielectric Properties of Anodic Films on Ti-W Alloys

H. Habazaki, M. Uozumi, H. Konno, K. Shimizu, S. Nagata, K. Takayama, Y. Oda, P. Skeldon and G. E. Thompson

Journal of the Electrochemical Society, **152**, B263-B270 (2005)

The influence of tungsten on an amorphous-to-crystalline transition, leading to formation of anatase, and dielectric properties is examined for anodic oxides on Ti-W alloys. The structural change, which occurs at voltages of similar to 10 V on high-purity titanium, and provides sites for generation of high-pressure gas oxygen bubbles, is suppressed to progressively increased voltages by increasing tungsten content of the film. Phosphorus species, derived from the electrolyte, also hinder the change. The tungsten species are located in the inner similar to 80% of the film thickness as result of the faster migration of Ti^{4+} ions relative to that of W^{6+} ions in the growing oxide. Although the reported permittivity of anodic tungsten oxide is higher than that of amorphous anodic titania, the permittivity of the films on alloys decreases gradually with increasing tungsten content.

Inter-Relationship between Structure and Dielectric Properties of Crystalline Anodic Zirconia

H. Habazaki, K. Shimizu, S. Nagata, K. Asami, K. Takayama, Y. Oda, P. Skeldon and G. E. Thompson

Thin Solid Films, **479**, 144-151 (2005)

Crystalline anodic oxide films have been formed on sputter-deposited zirconium and Zr-Ti alloys in 0.1 mol dm^{-3} ammonium pentaborate electrolyte, with their structure, composition, dielectric properties and growth behaviour examined using X-ray diffraction, transmission electron microscopy, Rutherford backscattering spectroscopy, glow discharge optical emission spectroscopy and electrochemical impedance spectroscopy. The films formed on zirconium consist of a high-temperature stable ZrO_2 phase (cubic or tetragonal) as well as monoclinic ZrO_2 , with the latter predominant with increasing formation voltage. The incorporation of titanium species into the films stabilizes the high-temperature phase up to high voltages. Associated with the change in the crystalline structure with the incorporation of titanium species, the permittivities of the oxides increase, in agreement with the higher permittivity of bulk cubic and tetragonal ZrO_2 containing stabilizing cations compared with that of bulk monoclinic ZrO_2 . The transport number of cations during crystalline oxide growth is about 0.05, irrespective of titanium incorporation.

Growth of Anodic Oxide Films on Oxygen-Containing Niobium

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

Electrochimica Acta, **50**, 5334-5339 (2005)

The present study is directed at understanding of the influence of oxygen in the metal on anodic film growth on niobium, using sputter-deposited niobium containing from about 0-52 at.% oxygen, with anodizing carried out at high efficiency in phosphoric acid electrolyte. The findings reveal amorphous anodic niobia films, with no significant effect of oxygen on the field strength, transport numbers, mobility of impurity species and capacitance. However, since niobium is partially oxidized due to presence of oxygen in the substrate, less charge is required to form the films, hence reducing the time to reach a particular film thickness and anodizing voltage. Further, the relative thickness of film material formed at the metal/film interface is increased by the incorporation of oxygen species into the films from the substrate, with an associated altered depth of incorporation of phosphorus species into the films.

Synthesis of Nano-Carbon Materials Using a Porous Alumina Template Formed by Anodizing of Etched Aluminum Foil

H. Habazaki, M. Hayashi, H. Konno and M. Inagaki

Journal of Surface Finishing Society Japan, **56**, 352-353 (2005)

Anodizing an etched aluminum foil with square tunnel pits in sulfuric acid for 1 h almost totally converts the foil to porous Al_2O_3 . A number of nano-pores (ca. 20 nm in diameter) are developed from the pit walls. Carbon nano-materials of unique “test tube brush” type morphology can be synthesized simply by heating a mixture of the template and polyvinyl chloride (PVC), since PVC is converted to liquefied pitch-like intermediate with low viscosity during heating in an inert atmosphere.

Recent Development of Highly Corrosion Resistant Bulk Glassy Alloys

K. Asami, H. Habazaki, A. Inoue and K. Hashimoto

Materials Science Forum, **502**, 225-230 (2005)

Recent development of corrosion resistant bulk glassy alloys such as Zr-, Fe-, Ni- and Cu-base alloys were presented. It was clarified that the enrichment of cations in the passive film, which is responsible to corrosion resistance, depends on both alloy compounds and environment. TEM observation also made it clear that alloys lose their advantageous properties such as corrosion resistance when they are devoid of or lose amorphous structure even in part due to low glass forming ability or heating. These findings were essentially similar to those of conventional amorphous alloys.

Behaviour of Zinc in Electropolished and Etched Al-Zn Alloys and Effect on Corrosion Potential

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

Corrosion Science, **47**, 2321-2331 (2005)

The enrichments of zinc developed in binary, solid solution Al-0.3at.%Zn, Al-0.4at.%Zn and Al-1at.%Zn alloys by electropolishing and alkaline etching are examined using Rutherford backscattering spectroscopy and medium energy ion scattering with additional interest in how such enrichments affect the corrosion potentials of the alloys. During alkaline etching in 0.1 M sodium hydroxide solution, significant enrichments of zinc arise in the alloy, similar to that achieved by an anodizing treatment. However, enrichment is unusually low following electropolishing in perchloric acid solution. Contrary to the effect of enriched copper in Al-Cu alloys, zinc enrichment has minor influence on the corrosion potentials of etched alloys in ammonium pentaborate solution, which remain roughly within +/-100 mV of those of non-enriched alloys.

Chromate Conversion Coatings on Aluminium-Copper Alloys

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

Corrosion Science, **47**, 341-354 (2005)

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 aluminium 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.

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 (2005)

Conversion coatings have been formed in two stages on sputtering-deposited aluminium 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 aluminium 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 behaviour 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.

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 (2005)

The unusual occurrence of anodic films of unlimited thickness has been recently reported for anodizing of tantalum in certain dehydrated, high-temperature electrolytes with organic solvents. The precise nature of these films is still uncertain. In the present work, non-thickness-limited (NTL) anodic films were formed at 0.1 mA cm^{-2} on aluminium and tantalum in glycerol/phosphate electrolyte at 453 K and then examined by Rutherford backscattering spectroscopy (RBS). The results disclosed films composed of alumina and tantala, free of phosphorus species at the resolution of the measurements. Most notably, the densities of the NTL alumina and tantala were about 2.4 and 3.6 g cm^{-3} , respectively. These values are less than those of compact anodic films of the type usually grown at high efficiency in aqueous electrolytes by respective factors of about 1.3 and 2.2. This difference in density is attributed primarily to the morphology and structure of NTL film materials, which incorporate significant porosity.

Oxidation Behavior of Plasma Sprayed Ni-Si Coatings on Carbon Steel Substrate

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

Advances in Applied Plasma Science, **5**, 187-192 (2005)

The Ni-Si coatings, with the main phases of NiSi₂ and NiSi, were deposited on the carbon steel through air plasma spraying. Isothermal oxidation tests of the carbon steel substrates with the Ni-Si coatings at 500°C to 800°C have been carried out. The results indicated that the SiO₂-based oxide scales, with the thickness of 120-520 nm, were formed on the surface of the coatings after oxidation at 500°C to 800°C for 100 hrs. During oxidation, phase transformation happened among the NiSi₂, NiSi and Ni₂Si phases inside the Ni-Si coatings, the reason of which has been studied. The growth mechanism of SiO₂ scales and the interface analysis between the coatings and substrates during oxidation have also been discussed respectively.

Interfacial Reaction between CrSi₂ Coatings and Steel in Oxidizing Atmosphere

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CrSi₂ coatings were deposited on steel by air plasma spraying. Isothermal annealing of the steel substrate with CrSi₂ coatings at 773 K to 1273 K in an oxidizing atmosphere was carried out, and the interface reaction between the steel substrate and CrSi₂ coatings was investigated. Formation of a reaction zone was observed only at 1273 K and the structure of the reaction zone was speculated to be CrSi₂/Cr-Si-Fe/Fe₂Si/Fe₂SiO₄/steel. In addition, thermal cyclic annealing (RT-1273 K) led to occurrence of cracks in the CrSi₂ coatings, resulting in formation of nodule-like iron oxide on the coatings. On the other hand, no formation of reaction zone was observed. These results demonstrate that the proposed coating system is proof against oxidizing atmosphere below 1073 K. (in Japanese)

TDS Measurement of Hydrogen Released from Cr₂O₃ Scale Formed in N₂-O₂-H₂O Atmospheres

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Thermal desorption spectroscopy, glow discharge optical emission spectroscopy, and Vickers microhardness measurements of a Cr₂O₃ scale formed on stainless steel were performed to clarify the effect of dissolved hydrogen on deterioration of a Cr₂O₃ scale. In addition, the evaporation of Cr₂O₃ caused by the reaction with water vapor was also investigated. TDS measurements demonstrated that the amount of dissolved hydrogen increased with increase in H₂O concentration in an oxidizing atmosphere and then became almost constant, and the maximum amount of dissolved hydrogen in a Cr₂O₃ scale was estimated to be about 0.4 mol %. GD-OES measurement showed that hydrogen existed near the oxide scale/substrate interface. On the other hand, the results of Vickers hardness measurements demonstrated that dissolved hydrogen in a Cr₂O₃ scale has little effect on mechanical degradation of the Cr₂O₃ scale. It was therefore concluded that evaporation of Cr₂O₃ rather than dissolved hydrogen in the Cr₂O₃ scale is the main factor responsible for deterioration of the Cr₂O₃ scale.

Improvement of Oxidation Resistance of NbSi₂ by Addition of Boron

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Materials Science Forum, **502**, 243-248 (2005)

NbSi₂ is a promising candidate as a coating material for Nb-base alloys. However, it shows complex oxidation behavior, depending on oxidation temperature. In the present study, in order to clarify the oxidation resistance of NbSi₂, oxidation tests of sintered NbSi₂ were carried out at temperatures ranging from 773 to 1673 K in air. Moreover, the effect of addition of boron on oxidation resistance of NbSi₂ was clarified. NbSi₂ showed accelerated oxidation at temperatures of 1073 K and above. The accelerated oxidation was caused by formation of a porous oxide layer, which may be due to the phase transformation from amorphous to crystalline SiO₂. The addition of boron to NbSi₂ leads to the formation of a protective borosilicate layer, resulting in great improvement of the oxidation resistance. Consequently, NbSi₂ added boron shows excellent oxidation resistance till at least 1673 K.

Oxidation behavior of sulfidation processed TiAl-2at.%X(X=Si, Mn, Ni, Ge, Y, Zr, La and Ta) alloys at 1173K in air

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Intermetallics, **13**, 694-703 (2005)

The oxidation behavior of sulfidation processed TiAl-2 at.%X (X=Si, Mn, Ni, Ge, Y, Zr, La, and Ta) alloys was investigated at 1173 K in air for up to 630 ks under a heat-cycle condition between 1173 K and room temperature. During the sulfidation processing the TiAl-2 at.%Ta alloy formed Ta-aluminides on the TiAl₃ layer, while the alloys containing Mn, Ni, Y, and Zr formed a TiAl₃ (TiAl₂ included) layer including a small amount of the third element, like the TiAl binary alloy. The cross-sectional microstructure of the TiAl-2 at.%Ta alloy shows the sequence: oxide scale/TiAlTa/TiAl₂/alloy substrate; and the cross sections of the alloys containing Mn, Ni, Y, and Zr are: oxide scale/Ti₃Al/alloy substrate. The TiAl-2 at.%Ta alloy showed some scale exfoliation at the initial stage of oxidation, but very little exfoliation after long oxidation times, whereas alloys containing other third elements such as Si and Ge showed little exfoliation at the first several cycles and then tended to exfoliate significantly, resulting in very rapid oxidation. The TiAlTa/TiAl₂ layers formed by the reaction between the Ta-aluminide and TiAl₃ improve the oxidation properties of the TiAl-2 at.%Ta alloy.

α -NiPt(Al) and Phase Equilibria in the Ni-Al-Pt System at 1150 °C

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The α -NiPt(Al) phase and its associated equilibria in the Ni-Al-Pt system at 1150 °C were investigated by analyzing equilibrated bulk alloys and the interdiffusion zones of diffusion couples. Phase constitutions, tie-lines and microstructures were determined using a combination of techniques, including high-energy synchrotron X-ray diffraction, scanning electron microscopy and electron probe microanalysis. A large Pt solubility limit was found to exist in the β -NiAl, \sim 42 at.%, and in γ' -Ni₃Al, \sim 32 at.%. The α -NiPt(Al) phase was found to have wide Pt solubility range of about 33–60 at.% and to skew along an almost constant Pt/Al ratio of 1.5. The α -NiPt(Al) has an ordered face-centered tetragonal L1₀ crystal structure, with the Al and Pt atoms found to be preferentially located in the corners and prismatic faces, respectively. The temperature dependence of the lattice parameters and unit cell volume of the α phase were also determined.

Interdiffusion Behavior of Pt-modified γ -Ni + γ' -Ni₃Al Alloys Coupled to Ni-Al-based Alloys

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Metallurgical and Material Transactions. A, **36A**, 1769-1775 (2005)

The effect of platinum addition on the interdiffusion behavior of γ -Ni + γ' -Ni₃Al alloys was studied by using diffusion couples comprised of a Ni-Al-Pt alloy mated to a Ni-Al, Ni-Al-Cr, or Ni-based commercial alloy. The commercial alloys studied were CMSX-4 and CMSX-10. Diffusion annealing was at 1150 °C for up to 100 hours. An Al-enriched γ' -layer often formed in the interdiffusion zone of a given couple during diffusion annealing due to the uphill diffusion of Al. This uphill diffusion was ascribed to Pt addition decreasing the chemical activity of aluminum in the γ + γ' alloys. For a given diffusion couple end member, the thickening kinetics of the γ' layer that formed increased with increasing Pt content in the Ni-Al-Pt γ + γ' alloy. The γ' -layer thickening kinetics in diffusion couples with Cr showed less of a dependence on Pt concentration. Inference of a negative effect of Pt and positive effect of Cr on the Al diffusion in this system enabled explanation of the observed interdiffusion behaviors. There was no or minimal formation of detrimental topologically close-packed (TCP) phases in the interdiffusion zone of the couples with CMSX-4 or CMSX-10. An overlay Pt-modified γ + γ' coating on CMSX-4 showed excellent oxidation resistance when exposed to air for 1000 hours at 1150 °C. Moreover, the Al content in the coating was maintained at a relatively high level due to Al replenishment from the CMSX-4 substrate.

Changes of an Outer β -NiAl and Inner α -Cr Coating on Ni-40at%Cr Alloy During Oxidation at 1373K in Air

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Oxidation of Metals, **64**, 119-130 (2005)

Formation mechanisms of a coating with a duplex layer, outer β -NiAl(Cr) and inner α -Cr(Ni) layer structure on a Ni-40.2 at% Cr alloy were proposed and change in the coating structure was investigated during high temperature oxidation. The Ni-40.2 at% Cr alloy was electro-plated with about 12 μ m Ni followed by a high Al activity pack cementation at 1073K to form a coated layer with an outer δ -Ni₂Al₃ and an inner layer containing Al more than 70at% which grew with an inward diffusion of Al. The coated Ni-40.2 at% Cr alloy was oxidized at 1373K in air for up to 2592 ks. It was found that at the initial stage of oxidation the as-coated layer structure changed to a two-layer, outer β -NiAl(Cr) and inner α -Cr(Ni), structure. Al contents in the α -Cr(Ni) layer was less than 0.3 at%. With long term oxidation an intermediate γ -Ni(Cr, Al) layer formed between the outer and inner layers, whereas the inner α -Cr(Ni) layer became thinner and then disappeared after the 2592 ks oxidation at 1373 K. Coating processes and changes in the coating structure during high temperature oxidation were discussed based on diffusion and composition paths plotted on a Ni-Cr-Al phase diagram.

The Role of Bond Coat in Advanced Thermal Barrier Coating

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A novel diffusion barrier bond coat with a duplex layer structure, a sigma phase Re-Cr-Ni barrier and Ni aluminides as an aluminum reservoir was formed on a Ni based superalloy (TMS 82+) and Hastelloy X. The oxidation behavior of both alloys with and without the sigma-Re-Cr-Ni phase as a diffusion barrier was investigated at temperatures of 1373K (Hastelloy X) and 1423K (TMS-82+) for up to 360ks. It was found that the Re-Cr-Ni act as a diffusion barrier for both inward diffusion of Al and outward diffusion of alloying elements in the alloy substrate.

Development of Re-based diffusion barrier coatings on nickel based superalloys

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A diffusion barrier type coating with a duplex layer structure, an inner δ -(Re, W, Cr, Ni) as a diffusion barrier and outer Ni-aluminide as an Al reservoir, was formed on a Nickel based, single crystal, superalloy (TMS-82+) and on Hastelloy X. Oxidation properties of both the alloys with or without the diffusion barrier coating were investigated in air under thermal cycling between room temperature and 1423 K for up to 360 ks. The inner δ layer with a composition (at%) of (35-40) Re, (15-20) W, (15-25) Cr and (15-25) Ni was produced by electrodeposition of Ni-70Re and Ni-20W films from aqueous solutions followed by Cr-pack cementation at temperatures between 1473 and 1573 K, and the outer Ni-aluminides of β -(Ni,Cr)Al + γ' -(Ni,Cr)₃Al was formed by electrodeposition of a Ni film, followed by Al pack cementation. After the 360 ks oxidation it was found that the structure and composition of both δ layer and alloy substrate were retained with little change. Furthermore, there was little Al in the δ layer. It could be concluded that the Re-based alloys such as δ (Re(W),Cr,Ni) are very promising candidates as a diffusion barrier between the outer Al-reservoir layer and alloy substrate at temperature of 1423 K. It was found that the Re(W)-Cr-Ni acts as a diffusion barrier for both inward diffusion of Al and outward diffusion of alloying elements in the alloy substrate.

Effect of alloy element addition on oxidation behavior of Ni-40Cr alloys coated with a duplex β -NiAl / α -Cr layer

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Zairyo-to-Kankyo, 54, 207-211 (2005)

A coating consisting of duplex layer of β -NiAl and α -Cr layer was formed on Ni-40Cr-3X (X (at%) = Ta, Nb, Ti, Zr, V, Ru, Rh, Re, Ir, and Pt) alloys by electroplating of Ni (12 μ m thick) and high Al-pack diffusion, followed by heat treatment in air at 1373K for 86.4ks. The coated alloys were oxidized in air for up to 2332.8ks under thermal cycling between 1273K and room temperature. Oxidation amounts increased and then turned to decrease with increasing oxidation time. The critical times became longer in the order of Ta, Ti, Nb, Pt, Ir, V, Re, Rh, and Ru except for Zr which showed no scale spallation. The alloy containing Zr was oxidized in accordance with parabolic rate law showing the rate constant of $1.2 \times 10^{-10} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-1}$, while the alloy containing Re showed significant spallation of the scale. It was found from the result after oxidation at 1373K for 2338.8ks that the α -Cr layer became thinner from 30 to 10 μ m for the Ni-40Cr-3at.%Zr alloy, whereas it was almost unchanged to be 20 μ m for the Ni-40Cr-3at.%Re alloy. It seems to be the reason for α -Cr stability that the α -Cr formed on the Ni-40Cr-3at.%Re alloy contains 8-10at%Re.

Preparation of Highly Functionalized Hydrotalcite for Drug Delivery Systems

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J. Jpn. Soc. Powder Powder Metallurgy, **52**, 857-860 (2005)

Intercalation of drugs into hydrotalcite has been expected to apply for drug delivery systems. Osteoblast was cultivated in the culture solution dispersing hydrotalcite-ATP intercalation compound. The cells expanded in volume after 3 h cultivation. Hydrotalcite was shown nontoxic and a part of it was incorporated in the osteoblast. It is necessary to make hydrotalcite crystals finer for endocytosis. Fine crystals of hydrotalcite ($< 50 \text{ nm } \phi$) were obtained by applying a strong magnetic field (5 T) in the direction vertical to the gravity during the precipitation of hydrotalcite from solution. Hydrotalcite with drugs in the interlayer is to be transferred to parts in the bodies targeted for therapy, and a control from outside the body is necessary. A composite of hydrotalcite with magnetite was prepared by firing hydrotalcite coated magnetite particles at 400°C in nitrogen atmosphere. A firm bond was established between them and the composite could be controlled by a magnet. (Japanese)

Compositional, Morphological, and Magnetic Modifications of Hydrotalcite for Drug Delivery

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Archives of BioCeramics Research, **5**, 142-145 (2005)

Hydrotalcite (HT), a layered double hydroxide of magnesium and aluminum, exchanges its interlayer anions with those in external solutions, and has been considered a potential vector for anionic pharmacological bio-molecules in drug delivery systems. As a vector the following modifications of HT were made: the effect of the order of addition of reagent solutions on the purity and crystallinity of HT was examined and a mixed solution of magnesium, and aluminum nitrates was added to an alkali solution to prevent the contamination by aluminum hydroxide. A strong magnetic field was applied to HT just after its precipitation, and this led to the formation of less aggregated plate-like small crystallites with better crystallinity. To make HT susceptible to magnetism for external control with magnets, a composite of HT and magnetite was produced by precipitating HT in the presence of magnetite particles and by fixation of HT to the magnetite with a thermal treatment. The HT-magnetite composite showed the ability to intercalate ATP. (English)

Dissolution Resistance of Rusts on Galvanized Steels in Atmospheric Environments

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Tetsu-to-Hagane, **91**, 706-711 (2005)

Detailed examinations of the corrosion processes of galvanized steels have shown that the steels exhibit some corrosion resistance after the zinc has corroded away. This corrosion resistance has been ascribed to a protective nature of the corrosion products from the zinc layer. Rusts exposed to environments containing air and water are subject to dissolution, and the protective components in the rust must be resistant to dissolution to persist and play a protective role in steels. In this investigation, zinc oxide, zinc carbonate, basic zinc carbonate, zinc ferrite, magnetite, and hydrated iron(III) oxide were chosen as model corrosion products, and their solubilities in water were examined as a function of pH. The solubilities of zinc oxide, zinc carbonate, and basic zinc carbonate are similar and very large, indicating that these would be dissolved away in atmospheric environments. The values of the solubility products of zinc ferrite and magnetite have not been reported and were estimated from thermodynamic data for the solubility calculations. The solubilities of zinc ferrite, magnetite, and hydrated iron(III) oxide are very much smaller than those for zinc oxide and carbonates. At pH lower than 7 the solubility order is: zinc carbonate ~ zinc oxide ~ basic zinc carbonate >> zinc ferrite > magnetite > hydrated iron(III) oxide. The compounds containing iron(III) ions are likely to show the adequate resistance to dissolution and to form the protective film. It is known that protective rusts are composed of fine particles of low crystallinity. The protective nature of these compounds can be explained by the effect of zinc ions on the crystallinity, particle size, and other properties of the compounds during their formation and growth. (Japanese)