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CONTENTS

Page

Current Activities and Presentations

Abstracts of Publications

Corrosion and Inhibitors

Passivation and Anodic Oxidation

Characterization of Surface and Interface

Electrometallurgy

High Temperature Oxidation and Sulfidation

Surface Finishing and Micro Fabrication

Joining and Interfacial Reaction

Nuclear Waste Disposal

Hydrogen Absorption / Release and Electrolysis Products in D_2

Ion Exchange

Materials Processing

Dental Materials

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Our research activities are concerned with corrosion and corrosion protection of metals, and development of recovery system of aluminum scrap.

Research programs in progress are as follows:

(1) Effect of Ultra Violet Light Irradiation on Titanium Anodic Oxide Films

Ultra violet (uv) laser light irradiation induces a damage of the protective oxide film on titanium. The damage of the oxide film was measured by ellipsometry and AC impedance technique. The simultaneous ellipsometric measurement during the irradiation was done in a cell with three optical windows, two of which was used for the ellipsometric measurement and the other for uv laser light irradiation. The changes of complex refractive index and thickness of the oxide films were estimated as a function of anodic bias relative to the flat band and of solution pH from the simulation of ellipsometric data . It was also found that the donor density in the film increases with irradiation of uv light from the Mott-Schottky plot of the impedance data. The change is caused by active holes in the oxide film induced by uv light irradiation.

(2) Semiconductive Properties of Passive Film

The protective oxide films on metals are one of important factors for understanding the corrosion phenomena of metals. The semiconductive properties of the oxide films were examined by measurement of electronic current from redox species in the aqueous solution on passivated iron and stainless steels. The iron passive films completely suppress electronic flow from Fe^{3+}/Fe^{2+} redox in the solution in the anodic potential region. This rectification effect is due to formation of space charge layer in the oxide film. The semiconductive properties were also examined by AC impedance and potential modulation reflectance.

(3) Corrosion Protection of Zinc by Conducting Polymer films

New protection films on zinc were studied which consist of conducting polymers of poly-pyrrole and polyaniline. The corrosion rate was estimated by measurement of polarization resistance for zinc electrode covered by polypyrrole and polyaniline occluding various sizes of anions. The conducting polymers occluding the anions with the larger size brings about the better corrosion resistivity probably due to inhibition of anionic transfer.

(4) Surface layers on metals in gaseous corrosion environments.

Surface layers initially formed on copper and iron in nitrogen or air containing sulfur dioxide and water vapor are being investigated by in situ techniques, such as IR-RAS and QCM. The components of the surface layer, which was formed on copper in air containing 10 ppm SO_2 and the relative humidity of 80%, were successfully determined by applying two-dimensional correlation analysis technique to in situ time-resolved IR-RAS spectra. Sulfite and sulfate grow in the surface and Chevreul's salt is estimated as the main component of sulfite and $CuSO_4 \cdot 5H_2O$, as that of sulfate, and the formation of an adlayer of water appears preceding sulfite and sulfate. The formation rate of sulfite is initially higher than that of sulfate, but the rate declines to become lower than that of sulfate.

(5) Corrosion behavior of binary tin alloys in an aqueous sulfuric acid.

In relation to the development of a lead free solder, corrosion tests of binary tin alloys (Sn-Zn, Sn-Bi and Sn-Ag) at the eutectic compositions, in a dilute sulfuric acid are in progress. The quantities of dissolved components of the alloys were determined together with surface analysis of the samples. The Sn component preferentially dissolves from Sn rich solid solution phases of Sn-Bi and Sn-Ag alloys and the Zn and Sn components dissolve from Sn-Zn alloy, but dissolution of Zn becomes inhibited.

(6) Development of corrosion inhibitors

The inhibition performance of newly-developed benzotriazole derivatives was evaluated for copper and copper alloys by immersion tests, electrochemical polarization as well as electrochemical ac impedance spectroscopy and SERS technique.

(7) Copper corrosion and its prevention

Mechanisms of the localized "ant's nest" corrosion in copper tubes for air-conditioning units were studied in a simulated atmosphere in the presence of volatile organic substances from woods.

(8) Electrorefining of scrap Aluminum in molten salts

Al scrap containing Fe, Zn and Cu as impurities was electrorefined by using a stacked bipolar cell in molten salt at 750 °C. Pure Al with 99.97-99.98% purity was recovered in a molten salt composed of $5\%AlF_3$-$7.5\%NaF$-$39.4\%NaCl$-$48.1\%BaCl_2$ (mol). Relation between operation current and cell voltage was examined experimentally and theoretically.

(9) Recovery of Aluminum from Aluminum dross

Recovery of metallic aluminum from aluminum dross comprised of Al alloy. Al oxides and other metal oxides was examined. The metallic aluminum was completely separated from the oxide components by floating of liquid metallic aluminum in a chloride-fluoride mixture molten salt.

Other Activities

The following foreign scientists visited this laboratory: Prof. Robert M. Corn, University of Wisconsin, Wisconsin USA on April 24, and Prof. Horacia Takashi Mishima and Prof. B. A. lopez de Mishima, Instituto de Ciencias Quimicas, F. A. A., Universidad Nacional de Santiago del Estero, Argentine on November 9-13.

Dr. Ueda attended the 193rd Electrochemical Society Meeting which was held in San Diego, U.S.A, in May and presented a paper entitled " Electrorefining of Aluminum Containing 1mass% Fe Using a Bipolar Electrode Cell".

Dr. Notoya participated in the 6th Conference of University of Science and Technology Beijing and Hokkaido University in Beijing, China in September. By request he lectured to students on "Copper and Culture" at three National Technical Colleges in Kushiro , Asahikawa in November and Tomakomai in December.

Presentations

The Role of Cr Component for Corrosion Resistance - Redox Characteristics and Temperature Dependency-; T. Ishikawa: The Joint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn, Surf. Finish. Soc. Jpn, and Jpn. Soc. Corros. Eng. Sapporo, Jan., 1998.

Effect of Rotation of a Cathode on Output Power Characteristics of $Al\text{-}Cl_2$ Chemical Cell; K. Imasawa, M. Ueda, S. Konda, T. Sasaki and T. Ishikwa: ibid.

Quantitative Analysis of Surface Layers Formed on Copper with in situ IR-RAS and QCM; J. Itoh, T. Sasaki and T. Ishikawa: ibid.

In situ IR-RAS Measurement of Surface Layers on Iron in Corrosive Gas Environment; T. Miyano, T. Sasaki and T. Ishikawa: ibid.

Corrosion Protection of Copper Wires with Benzotriazole by using High Pressure Water Jet (3); T.Tomitsuka,N.Tanabe and T.Notoya:The 121st Annual Meeting of Jpn. Inst. Metals., Tokyo, Mar.,1998.

Localized "Ant's Nest" Corrosion in Copper Tubes by Aldehydes; T. Notoya: ibid.

Behavior of Anodic Oxide Films on Titanium under Ultra Violet Irradiation by ellipsometry; T. Otsuki and T. Ohtsuka: The 65th Annual Meeting of Eletcrochem. Soc. Jpn. , Tokyo, April 1998.

Invesitigation of Electrorefining of Liquid Al Using a Stacked Bipolar Electrode Cell; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: ibid.

Change of Anodic Oxide Films on Titanium with Ultra Violet Irradiation; T.Ohtsuka and T. Otsuki: The Summer Joint Meeting of the Hokkaido Section. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, July, 1998.

Aldehydes and Ketones as Corrosives for Localized Corrosion in Copper Tubes; T. Notoya: ibid.

Adsorption Behavior of Thiourea on Gold Electrode; N. Yuuki, T. Sasaki and T. Ohtsuka: The 45th Disccusion Meeting of Jpn. Soc. Corros. Eng., Kanazawa, Aug., 1998.

Recovery of Aluminum Scrap by Electrolysis in Molten Salts; M. Ueda, S. Konda,

T. Sasaki and T. Ohtsuka: ibid.

IR-RAS In situ Measurement of Copper Surface Corroded in Moist Air; J. Itoh, T. Sasaki and T. Ohtsuka: ibid.

Tow-Dimensional Infrared Spectroscopy for Copper Surface Films Formed in Air Containing SO_2; J. Itoh, T. Sasaki and T. Ohtsuka: ibid.

Corrosion Behavior of Tin Alloys in Sulfuric Acid Solution; M. Mori, T. Sasaki and T. Ohtsuka:ibid.

Ant's Nest Corrosion in Copper Tubes by Alkylaldehydes and Alkylketones; T. Notoya: ibid.

Influence of Light Illumination on Anodic Oxide Films on Titanium; T. Otsuki and T. Ohtsuka:ibid.

Effect of UV Light Irradiation on Optical Property of Ti Anodic Oxide Films by Ellipsometry; T. Ohtsuka and T. Otsuki: Intern. Symp. on Electrochemistry of Ordered Interfaces, Sapporo, Sept., 1998.

Surface Layers Initially Formed on Cupper in Air Containing Water Vapor and SO_2 as Determined by IR-RAS; J. Itoh, T. Sasaki and T. Ohtsuka: ibid.

Vectorial Electron-Transfer Modified with Quinone Self-Assembled Monolayers on Gold Electrode; M. Nagata, M. Nango and T. Ohtsuka: ibid.

Self-Assembly and Characterization of Porphirine Derivatives on a Gold Electrode; T. Yamada, M. Nango and T. Ohtsuka:ibid.

Initial Layer of Zn-Ni Alloy Deposition on Au by Ellipsometry; T. Ohtsuka and A. Komori: The 49th Annual Meeting of Intern. Soc. of Electrochemistry, Kitakyushu, Sept., 1998.

Electron Transfer of Porphyrins and Quinones at Interfaces; M. Nango, T. Yamada, M. Nagata and T. Ohtsuka: ibid.

Change of Anodic Oxide films on Ti due to UV light Irradiation by Ellipsometry; T. Ohtsuka and T. Otsuki:ibid.

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Effect of Polishing on Growth Rate of the Initial Corrosion Layer on Copper; J. Itoh, T. Sasaki and T. Otsuka: The 98th Annual Meeting of Sur. Finish. Soc. Jpn., Akita, Oct., 1998.

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Electrorefining of Al by a Stacked Bipolar Cell; T. Ohmura, M. Ueda, S. Konda, T. Sasaki and T. Ohtsuka: The 30th Meeting of Molten Salt Chemistry, Osaka, Nov., 1998.

Recycle of Aluminum Scrap by using Cell Reactions; S. Konda, T. Sasaki, T. Ohtsuka and T. Ishikawa: Research Meeting on Material and Environment in Institute of Material Research of Tohoku University, Sendai, Nov., 1998.

Ant'sNest Corrosion in Copper Pipes with Aldehydes and Ketones; T. Notoya, K. Kawano and T. Ando: The 38th Meeting of Japan Copper and Brass Research Association, Tokyo, Nov., 1998

Inhibition of Copper Corrosion with 4- and 5-Carboxybenzotriazole; N. Huynh, T. Notoya, S.E. Bottle, V. Otieno-Alego and D.P. Schweinsberg: Corrosion & Prevention 98, Hobert, Australia, Nov., 1998.

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Our research activities are in developing materials with functions of corrosion resistance, separation, photo-electrochemical conversion, and others, where the methods of characterization and evaluation of the properties of the materials, in relation to surface reactions, surface compositions, and surface morphologies, are also being developed.

The research programs in our laboratory are:

(1) Preparation and characterization of γ-FeOOH

Iron oxyhydroxide γ-FeOOH is a compound found in the rust layers of well functioning steels resistant to weathering. Here, γ-FeOOH was prepared by oxygenation of Fe(II) salt solutions with different pH and concentrations to establish conditions under which this oxyhydroxide is formed. The product γ-FeOOH was examined by thermal analysis, XRD, and BET specific surface area measurements. It was found that γ-FeOOH formed in the pH region 6-8, and that the crystallite size was the largest at pH 7 and the specific surface area the smallest at pH7.5. The crystallite size increased with increasing Fe(II) concentration and aging time.

(2) Preparation and characterization of spinel type manganese oxide

A spinel type manganese oxide ($\square Mn_2O_4$) with vacancies ($\square$) is a "lithium ion memory" template ion exchanger, and has shown promise for the recovery of lithium from sea water and for preliminary concentration of trace lithium in natural environments. It was found that the incorporation of Li into the oxide results in the reduction of Mn(IV) to Mn(III), and that the incorporation rate decreases steadily with increases in the backward reaction. A rate equation derived by modeling the reaction reproduced the observed results well, and can be used to assess and predict the amount of incorporation for given conditions.

(3) Ion exchange properties of metal oxide corrosion products and hydroxyapatite as an ion separator

Both metal oxides and hydroxyapatite have ion-exchange properties due to surface hydroxyl groups formed by dissociative chemisorption of water molecules. For solid/solution interphase reactions like ion exchange, the mass-action law cannot be applied simply because of lateral interactions between adsorbed ions. We have been applying the Frumkin isotherm for such systems, and evaluation and characterization of the ion-exchange properties of these materials are being made.

(4) Dissolution of metal oxides in chelating agent solutions

The structural components of cooling systems of (nuclear) power plants are covered with metal oxides as corrosion products, and they cause inhibition of heat transmission and radioactive contamination due to incorporation of isotopes. The corrosion products are removed industrially by dissolution with chelating agents. The rate of dissolution of CuO in EDTA solutions was measured as a function of pH and EDTA concentration. It was found that the concentration of dissolved Cu increased linearly with time for low pH (≤ 7) while the concentration-time curves for high pH (≥ 8.5) were parabolic, and that the dissolved concentration at 5 h showed a peak at pH 7~8. Our dissolution model developed for magnetite was applied, here EDTA attacks on lattice Cu ions combined with proton attacks on lattice oxide ions are considered. The derived rate equation reproduced the behavior of CuO dissolution with EDTA well.

(5) REM effect on high temperature oxidation of Fe-Cr alloys

The favorable effect of REM on high temperature oxidation of chromia forming alloys is well known but no explanation of the effect is established. In this study, oxidation of Fe-16Cr alloys with lanthanum hydroxide coatings was carried out at 1373 K. It was found that the growth rate and the time to rupture of the scales are improved with 10^{16} atom cm^{-2} of coating. The value is similar to a reported one at which the growth of oxide scales changes from predominantly cationic to anionic transport. Iron rich oxide particles formed initially and converted to a chromium rich layer. This cannot be explained by the nucleation model, and the change in growth mode of oxide scale seems to be the reason for the REM effect.

(6) Initial stage of the high temperature oxidation of low chromium alloys

Thin oxide scales initially forming on most heat resistant alloys sustain the corrosion resistance. However, the critical content of chromium to form chromium-rich scales on chromia forming alloys is not clear. In this study high temperature oxidation of Fe-Cr binary alloys containing 5 to 18 mass% was carried out at 1173 K for several seconds upto 5 minutes. Analysis of the oxide properties showed that the crytical content is 11 mass%. This value coincides with the transition from α to γ phase of the underlying alloys. It is suggested that the formation of chromium-rich scales is related to lattice diffusion of metallic species in the alloys.

(7) Oxide film formation at high temperature under constant stress

Thin oxide scales formed on Fe-16Cr alloy have been found to contain equal amounts of iron and chromium in past studies. Simultaneous ionization of iron and chromium at oxide/alloy interfaces is difficult to explain if outward migration of cations is predominant in the scale growth. It has been proposed that mechanical breakage due to growth stresses and restoration of the scales may occur during the growth caused by the formation of iron containing scales. To verify this mechanism, high temperature oxidation study of Fe-Cr alloys under tensile stress, which may counteract the growth stresses, is planned. Apparatus for the study has been installed and the work is now in progress.

(8) Preventing photo-electrochemical corrosion of zinc oxide

Zinc oxide has the potentials to oxidize substances in aquatic media at negative potentials under UV light because of its positive valence band level. However, photo-electrochemical corrosion of ZnO itself occurs in such a situation. Stable titanium oxide is added to ZnO and photo-electrochemical corrosion tests were carried out for several days. It was shown that the corrosion takes place in the early stage of the test and then stops, even when a high anodic current due to oxygen evolution reaction is maintained. A thin titanium oxide layer on the ZnO surface prevents the corrosion and protects the underlying ZnO to sustain the high anodic current.

Presentations

Evaluation of the Ion-Exchange Properties of Surface Hydroxyl Groups on Manganese Dioxide with Lattice Vacancies (λ-MnO_2); A. Tanaka, H. Tamura, and R. Furuichi: The 1998 Winter Joint Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1998.

Lateral Interactions between Divalent Heavy Metal Ions Adsorbed on the Surface of Metal Oxide Particles; H. Tamura and R. Furuichi: The 74th Spring Annual Meeting of Chem. Soc. Jpn., Kyoto, Mar., 1998.

Initial oxidation of Type 430 stainless steel at high temperatures; I. Saeki: The Forum on High Temperature Oxidation of Metals and Alloys, Iron and Steel Institute of Japan, Osaka, Apr., 1998.

Ion Adsorption Properties of Metal Oxides and Affinities of Ions for Oxides-Evaluation by Modeling; H. Tamura: The 5th Rust Science Seminar Sponsored by the Rust Science Society, Tsukuba, Apr., 1998.

Kinetics of the Incorporation of Li^+ Ions into Lattice Vacancies of λ-MnO_2 -A Model Considering a Backward Reaction; H. Tamura, A. Tanaka, and R. Furuichi: The 59th Symposium of Jpn. Soc. for Anal. Chem., Otaru, May, 1998.

Prevention of photoelectrochemical corrosion of semiconductor electrodes by doping; I. Saeki: The 16th Lilac Seminar, Hokkaido Branch of Electrochemical Society Japan, Otaki, Jun., 1998.

Improvements in Photoelectrochemical Corrosion Resistance of Thermally Formed Zinc Oxides by Titanium Inclusion; I. Saeki, J. Setaka, R. Furuichi: International Symposium of Electrochemistry of Ordered Interfaces, Sapporo, Sep., 1998.

A Kintetic Model for the Incorporation of Li^+ Ions into Lattice Vacancies of λ-MnO_2 -Examination of Forward and Backward Reactions Including Radicals; A. Tanaka, H. Tamura, and R. Furuichi: The 75th Autumn Annual Meeting of Jpn. Chem. Soc., Matsuyama, Sept., 1998.

High temperature oxidation of lanthanum hydroxide coated Type 430 stainless steel; A. Saito, I. Saeki, and R. Furuichi: The 136th Annual Meeting of Iron and Steel Institute of Japan, Matsuyama, Sep., 1998.

Surface Acid-Base and Charge Characteristics of Metal Oxide Particles and Affinities of Ions for Oxides; H. Tamura: The 101st Meeting of the Resources Processing Society of Japan, Sapporo, Oct., 1998.

Photoelectrochemical response of titanium-zinc-oxides; I. Saeki, H. Konno, and R. Furuichi: Annual Symposium of Material Research Institute, Tohoku University, Sendai, Nov., 1998.

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The current research activities of the laboratory are mainly concerned with corrosion of the metallic materials used in nuclear industry, development of fuel cells using reservoir alloys, estimation of pitting corrosion, thermal properties of cesium uranates and cesium chromate, and radioactive waste management.

Current research topics include:

Current Activities and Presentations

(1) The corrosion behavior of the candidate overpack materials in bentonite is being studied for safety assessment of the geological disposal of the high level radioactive waste. At present, average corrosion rates of iron and apparent diffusion coefficients of corrosion products have been determined, using neutron-activated iron foils and bentonite specimens with different dry densities. The corrosion rates and diffusion coefficients depend upon the dry density of the bentonite. Quantitative analysis of the corrosion products was also carried out using 1,10-phenanthroline as a colorimetric indicator to obtain the profiles of both Fe^{2+} and total Fe concentrations and of the Fe^{2+}/total Fe ratio. From the profiles, it is probable that the pH and/or redox potential of the pore water in bentonite can be changed by corrosion of iron.

(2) Migration of radionuclides in compacted bentonite, which is the most promising candidate for buffer material in geological disposal of the HLW, is considered to be dominated by diffusion because of its low permeability of water. In addition, significant retardation effects, caused by the high absorbing ability of bentonite, can be also expected when the radionuclides are cations. Therefore, the diffusion and sorption behavior are very important studies for performance assessment of the geological disposal, and have been extensively investigated. A pore water diffusion model, in which radionuclides are supposed to diffuse through free water in the pores of clay even at high clay dry density, has been generally adopted to explain the diffusion behavior. It is, however, pointed out that apparent diffusion coefficients were underestimated by the diffusion model at higher clay density. Also, surface diffusion, in which cations sorbed on clay migrate on the clay surfaces, has been proposed as an additional diffusion process. We have been studying the diffusion mechanism of radionuclides over a wide range of clay densities, by determination of the activation energies for the apparent diffusion coefficients of Na^+, Cs^+, Sr^{2+} and Cl^- ions in the compacted clays and by the XRD measurements of basal spacings of the compacted clays. Thus far we have seen evidence for changes in diffusion processes as a function of clay density. Pore water diffusion, surface diffusion and

interlayer diffusion appears to be dominant diffusion process at low, intermediate and high clay densities, respectively.

(3) Hydrogen gas is expected after the disposal of the HLW to be generated from corrosion of the overpack which is made of carbon steel. This could result in an increase in gas pressure inside of the buffer materials surrounding the overpack, since the buffer has high sealing ability. In order to ensure the long-term integrity of the repository, it is necessary to estimate the hydrogen evolution rate and to understand the migration behavior of the gas in the buffer materials. In these studies, the diffusion coefficient of helium gas in compacted montmorillonite was studied instead of hydrogen gas. Diffusion experiments for helium was carried out for water-saturated, compacted montmorillonite pellet at dry density of 1.0 Mg m^{-3} in distilled water, in which helium was saturated by bubbling. After a prescribed time, the montmorillonite pellet was sliced, and helium gas content in each slice was measured with QMS. The apparent diffusion coefficient of 0.9×10^{-11} m^2s^{-1} was obtained from the He concentration profiles. In addition, the amount of helium was found to be 0.5×10^{-6}g /g- water-saturated montmorillonite. This indicated that helium gas migrated in the compacted montmorillonite as dissolved gas, and that the migration was not affected by the sorption of the gas on the clay mineral.

(4) For safety assessment of land disposal of radioactive waste, the migration behavior of fission products and actinides in geologic formation must be clarified. In this connection, the stability constant of Sr^{2+} with humic acid was determined using ^{85}Sr as a radiotracer. Sorption coefficients of Sr^{2+} on kaolinite were measured by a batch method as a function of contact time, pH, and the concentrations of Sr^{2+} and humic acid (HA). The K_d values increased with pH under the conditions both with and without HA. The K_d values in the presence of HA remained virtually unchanged with increasing HA concentration up to several tens of ppm, in comparison with the values in the absence of HA. On the other hand, at higher HA concentrations, the K_d

values decreased with increasing HA concentration at pHs above 5. A model was proposed, in which the effect of HA on K_d of Sr (II) ions onto kaolinite was described in terms of the sorption coefficient of Sr(II) ions in the absence of HA , K_d^0; the sorption ratio of HA on kaolinite, f_{HA}; and the stability constant of Sr(II) humate,β. These parameters were treated as input data in the model calculation to obtain K_d as a function of pH and HA concentration. Despite the simple mathematical model, the K_d values estimated by the model calculation were in good agreement with the experimental data. This study has been applied to the system including Am(III) and Cm(III).

(5) Thermal expansion and thermal conductivity of cesium molybdate have been investigated. The temperature dependence of the lattice parameters of Cs_2MoO_4 was measured using high-temperature X-ray diffraction from room temperature to 773 K. The linear thermal expansion of Cs_2MoO_4 obtained from the temperature dependence of the lattice parameters was about 2% at 773 K, which was more than four times that of UO_2. The thermal diffusivity in Cs_2MoO_4 was measured by the laser flash diffusivity method from room temperature to 1000 K. Further, the thermal conductivity of Cs_2MoO_4 was evaluated from the measured thermal diffusivity, bulk density, and the literature value of the specific heat capacity. The thermal conductivity of Cs_2MoO_4 increased with temperature above 400 K, and was about 5% of that of UO_2 at 300 K and less than 20% at 1000 K. Further, the thermal properties of cesium uranates, Cs_2UO_4 and $Cs_2U_2O_7$, and their effects on the UO_2 fuel performances were investigated. The conditions of formation of the cesium uranates were estimated by the CHEMSAGE code. The cesium uranates were prepared from U_3O_8 and Cs_2CO_3, and identified by X-ray diffraction. The temperature dependence of the thermal expansion coefficients of Cs_2UO_4 and the thermal conductivity of $Cs_2U_2O_7$ were determined. It was found that there is an anisotropy between the thermal expansion coefficients in a- and c- axes, and their geometric mean was much larger than the thermal expansion coefficient of UO_2. The thermal conductivity of $Cs_2U_2O_7$ was smaller than that of UO_2, and it is anticipated

that the temperature of the UO_2 fuel appreciably rises when $Cs_2U_2O_7$ forms in the periphery of UO_2 pellets. Thermal expansion and thermal conductivity of Cs_2CrO_4 were also investigated.

(6) Electrochemical, chemical and other conventional techniques investigated hydrogen attack during strong cathodic electrolysis in the solution of metal and carbon. Hydrogen atoms interact very intensively with each other in the metal. Hydrogen concentration profiles were dependent on the condition of cathodic electrolysis and pre-treatment of metals. High level of hydrogen concentration in the surface layer was realized by electrolysis at high cathodic current density for a prolonged time. The rate of hydrogen absorption was influenced strongly by the formation of a layer having high hydrogen concentration. The hydrogenated layer of the metal induced strong embrittlement in the metals.

(7) Processes of passivation and localized corrosion of metals were studied with laser displacement equipment. The changes of displacement and reflection were simultaneously and continuously recorded with the change of corrosion current as the digital data. The displacement and the change of the reflection rate are strongly depended on the electrochemical potential for pure iron. It can be seen that the change mainly occurred at Flade potential during passivated process. For the case of pitting corrosion, the change occurred before pitting corrosion and these phenomena were also observed around the flat and smooth passive area as the pitting area.

Other activities

Research associate Dr. T. Mizuno attended the 7-th International Conference on Cold Fusion at Vancouver Canada in April 19-April-24, 1998. He attended the 33-th Intersociety engineering conference on energy conversion at Colorado Springs, Colorado in August 2-August 6, 1998.

Foreign researcher visited and joined the study in Nuclear Material System

Laboratory from April to September include Dr. A. Karabut from Scientific Industrial Association "LUTCH" Moscow Russia.

Professor Dr. H. Ohashi and Res. Assoc. Mr. T. Kozaki attended the workshop on the "Microstructural modeling of natural and artificially prepared clay soils with special emphasis on the use of clays for waste isolation" in Lund, Sweden, October 12-14, 1998.

Presentations

Dependence of the Displacement of Fe Electrode on Electrochemical Potential; Tadahiko Mizuno and Tomoko Maeda: The joint meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc., Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Jan.16 1998.

Heat evolution and Deposited Element during Glow Discharge of Metal Electrode in the Solution; Tadahiko Mizuno and Tadayoshi Ohmori: The joint Meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc., Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Jan.16 1998.

Intercomparison on Measurement of Distribution Coefficient (5) - Investigation on Differences of Measured Values between Individuals; Akiyoshi Saeki, Yasunori Mahara, Hiroshi Yasuda, Shigeo Uchida, Tomoyuki Takahashi, Shinichi Takebe, Hideo Kimura, Hideo Matsuzuru, Noriyuki Sasaki, Nobuo Ashikawa, Tamotsu Kozaki, Tatsuya Yajima, Takashi Nishi, Takuro Ohno, Masamitsu Toyohara and Mitsushi Motoyama, The 1998 Annual meeting of the Atomic Energy Soc. of Jpn., Higashiosaka, March 1998.

Intercomparison on Measurement of Distribution Coefficient (6) - Results and Discussion; Tomoyuki Takahashi, Shinichi Takebe, Hideo Kimura, Hideo Matsuzuru, Hiroshi Yasuda, Shigeo Uchida, Yasunori Mahara, Akiyoshi Saeki, Noriyuki Sasaki, Nobuo Ashikawa, Tamotsu Kozaki, Tatsuya Yajima, Takashi Nishi, Takuro Ohno, Masamitsu Toyohara and Mitsushi Motoyama, The 1998 Annual Meeting of the Atomic Energy Soc. of Jpn., HIgashiosaka, March 1998.

Probability of Neutron and Heat Emission from Pt Electrode Induced by Discharge in the Alkaline Solution; Tadahiko Mizuno, Tadayoshi Ohmori and Tadashi Akimoto, The seventh international conference on cold fusion, Vancouver, Canada, April 19-24,1998.

Detection of Radiation Emission, Heat Generation and Elements from a Pt Electrode Induced by Electrolytic Discharge in Alkaline Solution; Tadahiko Mizuno, Tadayoshi Ohmori and Tadashi Akimoto, The seventh international conference on cold fusion, Vancouver, Canada, April 19-24,1998.

Strong Excess Energy Evolution, New Element Production and Electromagnetic Wave and/or Neutron Emission in the Light Water Electrolysis with a Tungsten Cathode; Tadayoshi Ohmori and Tadahiko Mizuno, The seventh international conference on cold fusion,Vancouver, Canada, April 19-24,1998.

Detection of Radiation Emission, Heat Generation and Elements from a Pt Electrode Induced by Electrolytic Discharge in Alkaline Solutions; Tadahiko Mizuno, Tadayoshi Ohmori, Tadashi Akimoto and Yoshiaki Aoki, Intersociety of energy conversion engineering conference, Colorado springs, Colorado, USA, August 2-6, 1998.

Migration Behavior of Na^+ and Cl^- ions in Loosely Compacted Montmorillonite; Koichi Inada, Nobuhiko Saito, Atsushi Fujishima, Tamotsu Kozaki, Seichi Sato and Hiroshi Ohashi, The 1998 Fall Meeting of The Atomic Energy Soc. of Jpn., Fukui, Sept., 1998.

Diffusion Mechanism of Cesium Ions in Compacted Montmorillonite; Tamotsu Kizaki, Hiroki Sato, Seichi Sato and Hiroshi Ohashi, Workshop on the microstructural modeling of natural and artificially prepared clay soils with special emphasis on the use of clays for waste isolation, in Lund, Sweden, October 12-14, 1998.

Effect of Particle Size on the Diffusion Behavior of Radionuclides in Compacted Bentonite;Yuichi Sato, Mamoru Nakajima, Tamotsu Kozaki, Seichi Sato, Hiroshi Ohashi and Hiroyasu Kato, The 16th Meeting of The Hokkaido Secs. of The Atomic Energy Soc. of Jpn., Sapporo, Dec., 1998.

Adsorption of Am(III) and Cm(III) on Kaolinite as a Function of Humic Acid Concentration; Mohammad Samadfam, Takashi Jintoku, Seichi Sato, Hiroshi Ohashi, Toshiaki Mitsugashira, Mitsuo Hara, Yoshimitsu Suzuki, The 1998 Annual Meeting of the Atomic Energy Society of Japan, Higashi-osaka, March, 1998.

Stability Constants of Am(III) and Cm(III) with Humic Acid; Mohammad Samadfam, Takashi Jintoku, Tomofumi Sakuragi, Seichi Sato, Hiroshi Ohashi, Toshiaki Mitsunaga, Mitsuo Hara, Yoshimitsu Suzuki, The 1998 Fall Meeting of the Atomic Energy Society Japan, Fukui, Sep., 1998.

Diffusion Coefficient of Helium in Compacted Sodium Montmorillonite; Teppei Otsuka, Yasuhiro Kuroda, Seichi Sato, Hiroshi Ohashi, The 1998 Fall Meeting of the Atomic Energy Society Japan, Fukui, Sep., 1998.

INTERFACIAL ELECTROCHEMISTRY LABORATORY

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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 :

Current Activities and Presentations

(1) Measurement of Changes in Surface Energy of Gold Electrode by a Laser Beam Deflection Method

A laser beam deflection method which is capable of measuring absolute values of changes in surface energy was applied to a gold electrode in perchlorate solutions with and without iodide ions. The potential of electrocapillary maximum or potential of zero charge (pzc) obtained by the laser beam deflection method was in good agreement with that obtained previously by a piezoelectric technique. The derivative of surface energy with electrode potential, $-(\partial\gamma^{s}/\partial E)$, was quite different from the surface charge density, q_{m}, obtained with integration of current density in the cyclic voltammogram, indicating that the simple Lippmann equation, that is, $-(\partial\gamma^{s}/\partial E) = q_{\mathrm{m}}$, did not hold. Particularly, the value of $-(\partial\gamma^{s}/\partial E)$ took a maximum near the potential at which the charge transfer of adsorbed iodide ions occured to form the iodine adlayer in spite of that q_{m} increased monotonously with increasing the potential. The above results obtained by the laser beam deflection method were also consistent with those obtained previously by the piezoelectric technique. The rapid decrease in $-(\partial\gamma^{s}/\partial E)$ after the charge transfer of adsorbed iodide ions is directly associated with the formation of the iodine adlayer. The discrepancy between $-(\partial\gamma^{s}/\partial E)$ and q_{m} was ascribed to the changes in surface elastic strain accompanied by the structural changes of the adlayer.

(2) Nanoindentation of the Titanium Surfaces Covered with Anodic Oxide Films.

Nanoindentation tests were performed to evaluate the mechanical properties of the titanium surfaces covered with anodic oxide films which were formed at different potentials in deaerated pH 8.4 borate, ph 6.9 phosphate, 0.1 M HCl or 0.1 M H_2SO_4 solution. The hardness of the titanium surfaces calculated from the unloading curves increased with increasing the film thickness until the film breakdown took place due to the film crystallization. After the film breakdown, the hardness decreased significantly.

(3) Selective Ion Permeability of Manganese Oxides Prepared with Electrosynthesis.

The membrane potentials of γ-MnO_2 and Mn_3O_4, which were electrochemically prepared on a platinum mesh, were measured in neutral aqueous solutions of KCl, KNO_3, NaCl and Na_2SO_4 at 25 °C to examine the transport numbers of the electrolyte ions in the Mn oxides. In these solutions, the cation transport numbers, t_+, in γ-MnO_2 were 0.62 - 0.73, which were larger than those (0.38 - 0.51) in the bulk solutions. On the other hand, the anion transport numbers, t_-, in Mn_3O_4 were 0.62 - 0.79. which were larger than those (0.49 - 0.62) in the bulk solutions.

(4) Evaluation of Heterogeneity of Passive Films on Iron and Titanium Electrodes by Scanning Electrochemical Microscopy.

Scanning electrochemical microscopy (SECM) was applied to evaluate the heterogeneity of a passive film formed on a pure iron electrode in deaerated pH 8.4 borate solution. A probe current image of SECM was measured with a tip generation / substrate-collection (TG/SC) mode in deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $Fe(CN)_6^{4-}$ as a mediator. The difference in thickness of passive films formed on two iron plates at different potentials could be evaluated from the probe current image.

In the case of passive films on polycrystalline iron, the probe current image of the passivated iron surface with distinctive crystal grains was composed of the patch patterns, the shapes of which coincided completely with the shapes of the substrate crystal grains. The probe current flowed above the grain surface oriented to {100} plane was less than that above the grain surface oriented to {110} or {111} plane. The grain orientation dependence of probe current was ascribed to the difference in thickness of passive films formed on the crystal grains.

(5) Development of Ion Gun in Liquid Phase for Local Breakdown of Passive Film

An ion gun in liquid phase for the investigation of precursor processes of pitting corrosion was realized by using a silver/silver chloride microelectrode. It was used to induce a local breakdown of the passive film on iron. This electrode was set as a probe electrode of a scanning electrochemical microscope (SECM).

A small amount of chloride ions was generated by cathodic polarization of the silver/silver chloride microelectrode and induced the local breakdown of the passive film formed on iron in deaerated pH 6.5 borate buffer solution. Moreover, the microelectrode could detect ferric ions dissolved at the initial stage of film breakdown.

(6) Electrochemistry of InP in HCl and H_3PO_4

The semiconductive electrode characteristics of n-type and p-type InP wafers were measuredin 1.0 M HCl and 0.3 M - 1.0 M H_3PO_4 and the flat band potential, Efb, and carrier density, N_D and N_A, of both type of InP were evaluated from Mott-Schottky plots of the space charge capacitance obtained with impedance measurements.

Moreover, the cathodic decomposition (corrosion) of n-type InP in 1.0 M HCl was investigated under cathodic polarization at - 0.8 V (SHE) and followed by anodic potential sweep. After the cathodic polarization, anodic current peak was observedat - 0.47 V (SHE) during the anodic potential sweep. The anodic current peak was ascribed to the anodic dissolution of In which was produced on InP surface due to the cathodic decomposition ($InP + 3 H^+ + 3 e^- \rightarrow In + PH_3$) at - 0.8 V (SHE).

(7) Stability of the Titanium Oxide Film in Deaerated Neutral Solutions

Stability of the anodic oxide film formed on titanium was examined by using cyclic voltammetry, impedance measurements, and AFM observation. Comparison of voltammogram and impedance data measured in bentonite contact water, quasi-bentonite contact water (containing sodium carbonate and sodium sulfate ions), borate solution, carbonate solution, and sodium sulfate solution showed that the sulfate ion has an important role for degradation of oxide film. For example, the anodic oxide film formed in sodium sulfate containing solutions loose its electric resistivity faster than the films formed in other solutions, when electrode was polarized around 0 V vs. R.H.E. Donor density of the former oxide film was also considerably larger that the others.

AFM observation indicated that the oxide films formed in sodium sulfate containing solutions show rather smooth surface, while the other films show growth of micro-crystalline. These result showed that the surfate ion is incorporated to the anodic oxide film at the film formation process, induces defects states, and prevents crystallization of oxide at aging.

(8) In-situ Monitoring of Hydrogen Absorption into Ti using Resistmetry

Development of hydrogen absorption into Ti is an important issue because it leads rupture of materials. Electric resistance of Ti foil, wire, and thin film was measured during galvanostatic cathodic polarization for hydrogen absorption at various current density in H_2SO_4 solution.

Increase in resistance accompanying with hydrogen absorption depended on the condition of specimen surface. For example, air-formed oxide film or anodic oxide film prevented hydrogen permeation at small cathodic current density, and removal of oxide film by etching pretreatment rose the hydrogen absorption rate. Good correlation was observed between resistance and electrode potential, rather than cathodic current density.

(9) Light Emission from metal electrodes during high voltage cathodic polarization

Light emission from the metal electrodes cathodically polarized at cell voltages higher than 100 V was investigated in various aqueous electrolyte solutions. The emission of light was observed when intense cathodic polarization caused the temperature of the Pt electrodes to exceed the boiling temperature of the electrolyte. A thin vapor layer was formed at the metal / electrolyte interface in which a high electric field ionized vapor molecules to generate the plasma state. The light emission was caused by a glow discharge at relatively low cell voltages and by a spark discharge at high cell voltages. The spectra of the emitted light were observed for various metals such as Fe, Cr, Ni, stainless steel, Al, Cu, Zn, aluminum alloys, Pd, Ag, etc. in various kinds of electrolyte solutions. The results showed sharp emission lines which could be assigned to the constituents of the electrolyte solution, electrode material and gaseous hydrogen evolved at the electrode.

Other Activities

From July 15 to September 11, Dr. Gyozo. Lang, Depertment of Physical Chemistry, Eotvos Lorand University, Budapest, Hungary visited this laboratory to conduct the research on determination of surface energy of solid electrodes by Hungarian-Japanese intergovernmental co-operation.

In September, Prof. M. Seo, Assoc. Prof. K. Azumi , Mr. K. Fushimi (Res. Assoc.), Dr. A. W. Hassel (JSPS Foreign Researcher), and Mr. K. Ueno (Ph.D. Student) attended the 49th Annual Meeting of ISE held in Kitakyushu, Japan to present the four papers entitled "Monitoring of Hydrogen Absorption into Titanium using Resistmetry", "Heterogeneity of Passive Films on Iron and Titanium Evaluated by a Scanning Electrochemical Microscope", "Local Surface Energy Measurement on Gold by a Piezoelectric Response Combined with a Scanning Droplet Method", and "Measurement of Changes in Surface Energy of a Gold Electrode in Aqueous Solutions Containing Iodide or Bromide Ions"

In November, Prof. M. Seo, Mr. K. Fushimi, and Mr. K. Ueno attended the 194th Meeting of ECS held in Boston, USA to present the three papers entitled "In-Situ Nanoindentation of a Single Crystal Iron (100) Surface Passivated in pH 8.4 Boric Borate Solution", "Use of Ion Gun in Liquid Phase for Local Breakdown of Passive Film on Iron", and "Measurement of Changes in Surface Energy of a Gold Electrode by a Laser Beam Deflection Method". Dr. A. W. Hassel extented his stay in this laboratory until October, 1999 for further development of the droplet method.

The following foreign scientists visited this laboratory : Prof. Robert M. Corn, University of Wisconsin-Madison, U.S.A. on April 24, Prof. G. Horanyi, Central Reserach Institute of Chemistry, Hungarian Acadmy of Science, Budapest, Hungary on September 4, Dr. U. Kamachi Mudali, India Gandhi Centre for Atomic Research, India on October 28, Dr. Patrik Schmuki, Swiss Federal Institute of Technology, Depertment of Material Science, LC-DMX on November 30.

Presentations

Selective Ion Permeability of Manganese Dioxide Electrochemically Synthesized; M. Ushito and M. Seo : The 1998 Joint Meeting of Hokkaido Sec. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Corros. Eng., Sapporo, Jan., 1998.

In-Situ Monitoring of Hydrogen Absorption into Titanium during Cathodic Polarization using Resistmetry; Y. Asada, K. Azumi, M. Seo and T. Mizuno : ibid.

Effect of Specially Adsorbed Halide Ions on Redox Reaction of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$; K. Ueno and M. Seo : ibid.

An EQCM Analysis of Corrosion Mechanism of Electroplated Iron Thin Film in Deaerated Phosphate Solution; M. Kurosaki and M. Seo : ibid.

Mechanical Properties of Nano-area of Passive Films on Carbon Steel and Pure Iron; K. Suzuki, K. Fushimi, K. Azumi and M. Seo : ibid.

Change in Electronic Property of Titanium Oxide Film with Immersion Period in Non-Oxidative Aqueous Solution; N. Yasui, K. Azumi and M. Seo : ibid.

Evaluation of Heterogeneity of Passive Film Formed on Polycrystalline Iron Electrode by a Scanning Electrochemical Microscope; K. Fushimi, K. Azumi and M. Seo : ibid.

AFM Observation of Aluminum during Double Zincate Pretreatment; Y. Fujishige, K. Azumi and M. Seo : ibid.

In-Situ AFM Observation of Metal Surface during Anodic Polarization; F. Nukaya, K. Azumi and M. Seo : ibid.

Observation of Defects of Passive Films on Titanium by a Scanning Electrochemical Microscope ; T. Okawa, K. Fushimi, K. Azumi and M. Seo : ibid.

Study on Energy Structure and Electron Transfer Reaction at the Contact Adsorption

Phase of Electrode Interface ; M. Seo and K. Ueno : The 2nd Symposium on Electrochemistry of Ordered Interfaces, Grant-in-Aid for Scientific Research on Priority Area from The Ministry of Education, Science, Sports and Culture , Osaka, Jan.,1998.

Influences of Anodic Oxidation and the Subsequent HF Treatment on Visible Luminescence of Porous Silicon; M. Saito, K. Shigyo, K. Azumi and M. Seo : The 1998 Winter Meeting of the Hokkaido Sec. of Jpn. Soc. Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1998.

Changes in Aluminum Alloy Potential and Weight During the Double-Zincate Process" (Award Lecture) ;K. Azumi, M. Seo and Leonard Nanis : The 97th Annual Meeting of Surf. Finishing Soc. Jpn., Tokyo, March 1998.

Changes in Visible Luminescence Characteristics of Porous Silicon by Combination of Anodic Oxidation and HF Treatment ; M. Saito, K. Shigyo, K. Azumi and M. Seo : ibid.

Evaluation of Heterogeneity of Passive Film on Steel Surface by a Scanning Electrochemical Microscope ; K. Fushimi, K. Azumi and M. Seo : The 135th ISIJ Meeting, Tokyo, April 1998.

K. Fushimi, T. Okawa, K. Azumi and M. Seo : " Application of Scanning Electrochemical Microscope to Passive Film on Iron and Titanium" : The 65th Annual Meeting of Electrochem. Soc. Jpn., Tokyo, April, 1998.

Measurement of Membrane Potential of Manganese Dioxide Electrochemically Synthesized ; M. Ushito and M. Seo : ibid.

Measurement of Absolute Values of Changes in Surface Energy of Gold Electrode by a Laser Beam Deflection Method ; K. Ueno and M. Seo : ibid.

In-Situ Monitoring of Hydrogen Absorption into Titanium Using Resistmetry ; Y. Asada, K. Azumi, M. Seo and T. Mizuno : The 1998 Annual Meeting of Jpn. Soc. Corros. Eng., Tokyo, May 1998.

The Scanning Droplet Cell : Experimental Results and Determination of the Potential Distribution ; A. W. Hassel and M. Seo : ibid.

Stability of Titanium Oxide Film in Deaerated Aqueous Environment ; N. Yasui, K. Azumi and M. Seo : ibid.

Observation of Passive Film on Iron and Titanium by s Scanning Electrochemical Microscope ; K. Fushimi, T. Okawa, K. Azumi and M. Seo : ibid.

Evaluation of the Heterogeneity of Corroding Surfaces by Scanning Electrochemical Microscopy ; M. Seo and K. Fushimi : Seminar of the Soc. of Materials Sci. Jpn.,Osaka, May, 1998.

Electrochemical Surface Imaging of Gold with a Scanning Droplet Cell ; A. W. Hassel and M. Seo : 2nd International Symposium on Electrochemical Microsystem Technologies, Tokyo, Sept., 1998.

Nano-Mechano-Electrochemistry of Iron (100) Surface in Solution ; M. Seo, M. Chiba and K. Suzuki : 49th ISE Pre-Symposium on Electrochemistry of Ordered Interfaces, Sapporo, Sept., 1998.

Study of Adsorption of Iodide and Bromide Ions on Gold by a Laser Beam Deflection Method ; K. Ueno and M. Seo : ibid.

Monitoring of Hydrogen Absorption into Titanium using Resistmetry ; K. Azumi, Y. Asada, M. Seo and T. Mizuno : The 49th Annual Meeting of ISE, Kitakyushu, Sept., 1998.

Heterogeneity of Passive Films on Iron and Titanium Evaluated by a Scanning Electrochemical Microscope ; K. Fushimi, T. Okawa, K. Azumi and M. Seo, P. James and W. H. Smyrl : ibid.

Local Surface Energy Measurement on Gold by a Piezoelectric Response Combined with a Scanning Droplet Method ; A. W. Hassel, K. Fushimi, K. Ueno and M. Seo : ibid.

Measurement of Changes in Surface Energy of a Gold Electrode in Aqueous Solutions Containing Iodide or Bromide Ions ; K. Ueno and M. Seo : ibid.

Influence of Iodide Ions on Reduction Reaction of $Fe(CN)_6^{3-}$ on Gold Electrode ; K. Ueno, Y. Serizawa and M. Seo : The Fall Meeting of Electrochem. Soc. Jpn., Nagaoka, Oct., 1998.

Nanoindentation of Iron (100) Surface Electrochemically Controlled ; M. Seo, M. Chiba and K. Suzuki : ibid.

In-Situ Nanoindentation of a Single Crystal Iron (100) Surface Passivated in pH 8.4

Boric Borate Solution ; M. Seo, M. Chiba and K. Suzuki : The 194th Meeting of ECS, Boston, Nov., 1998.

Use of Ion Gun in Liquid Phase for Local Breakdown of Passive Film on Iron ; K. Fushimi, K. Azumi and M. Seo : ibid.

Measurement of Changes in Surface Energy of a Gold Electrode by a Laser Beam Deflection Method ; K. Ueno and M. Seo : ibid.

Nanoindentation of Titanium Surffaces Anodically Oxidized ; M. Seo, F. Nukaya and K. Azumi : Research Meeting on Materials and Environment for the 21 Century, Institute for Materials Research, Tohoku University, Sendai, Nov., 1998.

DISSIMILAR MATERIALS INTERFACE ENGINEERING LABORATORY

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In March, Assoc. Prof. Yu Jinming returned to the Institute of Corrosion and Protection of Metals Academia Sinica, China. Mr.Luo Feng joined the laboratory as a visiting researcher from Institute of Corrosion and Protection of Metals, the Chinese Academy of Science in China. In April, Mr.Son Gun Su joined the laboratory as a visiting student from Chang Won University, Korea.

The research activities of the laboratory are directed to an understanding of high temperature corrosion mechanisms of super alloy, inter-metallic compounds and iron-based alloys, and development of the corrosion resistant alloys and corrosion protection of steels with a Zn-Al dipping method in sea-water front environments. The research activity is also directed to an understanding of the solidification mechanism of metals and Alloys.

Current topics on research are in the following:

(1) High temperature sulfidation of alloys

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

(2) Effect of Nitrogen Gas on High temperature Oxidation of Ti-Al alloys

High temperature Oxidation Behavior of Ti-Al intermetallic compounds was investigated in N_2 and O_2 gas Mixtures, and this was focused toward Effect of Nitrogen gas on Oxidation Properties of the TiAl alloy.

(3) Ceramic-Metal and Metal-Metal joinings

Silicon nitride ceramics were joined to metals using active alloy solders such as Ni-Cu-Ti and Ag-Cu-Ti, and the new bonding process was developed. Aluminum alloys were joined with a newly developed solder and corrosion behavior of the metal-metal joints was investigated in many solutions.

(4) TLP Bonding

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

(5) Ultrasonic micro-spectroscopy

Scanning acoustic microscope was used to determine the residual stress by making use of the principle concept basing on the measurement of SAW velocity and its change in stress. This novel method was successfully applied to the ceramic-metal joints, ion-exchanged glasses, and Ag-ion diffused layer in glasses.

(6) Galvanizing process of steels by hot Zn-Al and Al-Si dippings

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

(7) Characterization of thermal barrier coatings

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

(8) Pb-free solder

In order to design Pb free solder, change in microstructure and mechanical properties of Sn-Bi alloys during thermal cycle were investigated.

(9) Molecular dynamics simulation of grain boundary formation

The Structure and the properties of the grain boundary of iron were investigated by Molecular Dynamics Simulation. Change in properties such as grain boundary energy and grain boundary strength in relation to the crystal orientation difference were estimated.

(10) Computer simulation of grain structure formation of casting

A new method to simulate the grain structure formation in casting was investigated by combining Monte-Calro Method and heat transfer analysis.

Other activities

Professor Narita visited University of New South Wales, Australia, in January and presented a lecture on High Temperature Corrosion of Metals. Professor Narita attended the Japan-U.S.A. Workshop on Surface Treatment Technology held at Hawaii in October. Assoc. Prof. Ohsasa attended The Third Pacific Rim International Conference on Advanced Materials and Processing held at Hawaii in July, and presented a paper entitled "Reactive Sintering of NiAl and Simultaneous

Joining to Steel". Assoc. Prof. Ohsasa attended the 6 th Hokkaido University-Beijing Science and Thechnology University Joint Seminar held at Beijing in September, and presented a lecture entitled "Analysis of Solidification Path of Fe-Cr-Ni Ternary Alloy".

Presentations

Effect of Impurity Oxygen in Nitriding Properties of γ-TiAl and TiAl-Si Alloys; T.Narita, T.Watanabe, and T.Yoshioka: Hokkaido University-UNSW Joint Meeting on High Temp. Corros., Sydney ,Jan.,1998

Effects of Ceramic Strength and Bonding Layer Thickness on Fracture Strength of Si_3N_4 Ceramic-Joints; S.Hata and T.Narita: ibid.

Simulation to Predict the Solidification Structure due to Stochastic Modeling; K.Ohsasa: Annual meeting of Jpn. Soc. Promotion of Science, Kyoto, Jan.,1998.

Development of Sulfidation-Resistant Ni Base Alloy; C.Fang, T.Narita, H.Yakuwa and M.Miyasaka: Annual Meeting of Jpn. Soc. Corros. Eng., 1998.

Effect of a Minute Oxygen on High Temperature Nitriding of TiAl and TiAlSi Alloys; T.Narita, T.Watanabe and T.Yoshioka: ibid

Analysis of Transient Liquid Phase Bonding Process using Ternary Filler Metal; T.Shinmura, K.Ohsasa and T.Narita: Annual Meeting of Jpn. Inst. Metals., Tokyo, Apr.,1998.

Chloridation Behavior of Pure metals under N_2-Cl_2 Atomosphere; C.Fang, T.Narita, M.Noguchi, H.Yakuwa and M.Miyasaka: ibid

Change in Hardness of Sn-Bi Eutectic Solder Alloy due to Aging Treatment; Hu Jia Ning, H.Tanaka, O.Munekata, M.Taguchi and T.Narita: ibid.

Analysis of Grain Boundary Property of Iron by Molecular Dynamics Simulation; K.Ohsasa, T.Toyama and T.Narita: Annual Meeting of Iron and Steel Inst. Jpn., Tokyo, Apr.,1998.

NiAl Coating on Iron by Reactive Sintering ; K.Matsuura, K.Ohsasa, N.Sueoka and M.Kudoh: Annual Meeting of Jpn. Inst. Light Metals, May, 1998.

Development of a Sulfidation-Resistant Nickel-based Superalloy for FCC Power Recovery; H.Yakuwa, T.Narita, M.Kawasaki, M.Miyasaka, C.Fang, T.Go and S.Nakahama: Turbine Rotors, International Turbomachinary Symposium, Houston, Jun, 1998.

High Temperature Corrosion Under Extreme Environment - Roll of Oxidation, Sulfidation and Chloridation- ; T.Narita: Assignment Symposium of Jpn. Inst. Metals., Sendai, June,1998.

Introduction to High temperature Corrosion; T.Narita: Seminar on The Interface Science, Nippon Steel Corp.,July,1998.

Effect of Nitrogen on High Temperature oxidaiton of TiAl alloy ; T.Narita, Y.Mizuno, T.Watanabe, and T.Yoshioka : Hokkaido University-UNSW Joint Meeting on High Temp. Corros., Yoichi, July,1998.

Structures and Formation Behavior of Coating Layer in Zn-Al Hot-Dipped Steels; J.Tanaka : ibid.

Oxidation Properties of Fe-5mass%Al Alloy in O_2 and/or N_2, air at 1073K; S.Hayashi and T.Narita: ibid.

Effect of Mo,Ti,Al Addition on High Temperature Sulfidition of Ni Base Alloy at 873K and Low Sulfur Pressure; C.Fang, H.Yakuwa, M.Miyasaka, and T.Narita : ibid.

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Dr. M. Sakairi left for England at the end of January to take his sabbatical leave for one and half years as a postdoctoral fellow at UMIST. In March, Mr. D. Aguilar Armijo left for his mother country, Honduras, to work again at Catedratico University. In April, two young researchers, Mr. Y. S. Lee and S. J. Choi, joined from Changwon National University, Korea, as research associates.

The research activity of the laboratory is still directed to a better understanding of structure and properties of anodic oxide films on aluminum and its alloys, and of the corrosion resistant materials at high temperatures. Surface patterning of aluminum is also attempted by metal deposition after laser irradiation.

Current topics on research are in the following:

(1) Local Ni-P electroless plating on aluminum with a pulsed YAG Laser

Aluminum specimen covered with porous anodic oxide films was immersed in solutions containing Pd^{2+}, Cu^{2+}, Ni^{2+} and Ni^{2+} / $H_2PO_2^-$, and irradiated with a pulsed YAG laser to remove the oxide film locally. The specimen was transferred into a Ni-P electroless plating solution to examine the effect of laser irradiation solution on the deposition of Ni-P during electroless plating. Fine particles of metal, Pd, Cu, Ni, or Ni-P, were deposited on each specimen at the laser-irradiated area after laser irradiation, and affected the initial Ni-P deposition during the subsequent electroless plating. The Pd particles enhanced it most, and the Cu particles did not show any effect. The Ni-P particles showed an enhancement more than the Ni particles.

(2) Surface patterning of aluminum with laser irradiation and Au-electrodeposition.

Aluminum specimen covered with porous anodic oxide films was immersed in Au^{3+} ion containing solutions, and then irradiated with a pulsed YAG laser through a convex lens before cathodic polarization. By controlling the laser power and irradiation time, grooves with 30 μm width and 70 μm depth were produced in the metal substrate. A dense layer of Au was deposited in the groove initially to fill it from the bottom, and then expanded to the outside of groove.

(3) Formation of oxide films on aluminum after destruction of anodic oxide film by laser irradiation.

Aluminum specimen covered with porous and barrier type-anodic oxide films was immersed in 0.1 M phosphate solutions with different pHs, and irradiated with one pulse of laser under anodic polarization to destruct the oxide film. Anodic oxide film formation started at about 0.4 ms after laser irradiation in the phosphate solutions, independent of solution pH. At the very initial stage, the oxide film formation was accompanied with the film dissolution, and then the film formation kinetics followed the inverse logarithmic law. The dissolution rate of oxide films at the initial stage showed a minimum at pH 2 - 3, suggesting the formation of zero charge complexes, like $Al(OH)(H_2PO_4)_2$.

(4) Formation of anodic oxide films on aluminum with ultra high potential sustaining ability in diluted NaOH solutions.

Anodic oxide films were formed on aluminum in $5 \times 10^{-5} - 5 \times 10^{-3}$ M NaOH solutions at different c.d. During anodizing, anodic oxide films grew thicker, and the film growth was accompanied by the formation and repairing of many voids and imperfections in the oxide film. At the final stage, the growth of anodic oxide films was ceased by film breakdown, and the film breakdown potential became higher at lower solution concentration and lower c.d.

(5) Formation of Al / Ti-composite oxide films by MOCVD and anodizing.

Aluminum specimen was initially covered with TiO_2 film by a metal organic chemical vapor deposition (MOCVD) and then anodized galvanostatically in a neutral borate solution. During MOCVD, the temperature, T_{TPT}, of tetra-iso-propyl titanate was controlled between 20 and 120 °C to change the deposition rate of TiO_2. Anode potential, E_a, increased linearly with time, t_a, and the slope of the E_a vs. t_a curve became flatter with increasing T_{TPT}. The electric capacitance of the anodic oxide films formed on specimens coated with TiO_2 was higher by 50 % than that on the specimen without TiO_2 coating, independent of T_{TPT}.

(6) Formation of Al / Zr- composite oxide films by sol-gel coating and anodizing.

Aluminum specimen covered with porous-type anodic oxide films was initially coated with Zr-oxide by sol-gel coating with a zirconium alkoxide / ethanol mixture, and then anodized galvanostatically in a neutral borate solution. During sol-gel coating, Zr-oxide filled partly the pores of porous oxide film, and deposited on it. During anodizing of the Zr-oxide coated specimen, the pore unfilled with Zr-oxide was filled with Al_2O_3 to produce Al-Zr composite oxide layer. The electric capacitance of the anodic oxide film produced thus was 20 % higher than that on electropolished specimen without Zr-oxide coating.

(7) Structural change in anodic oxide films on aluminum during potentiostatic anodizing.

Aluminum specimens 1) electropolished, 2) covered with a porous anodic oxide film, and 3) covered with a hydroxide film were initially anodized galvanostatically up to $E_a = 300$ V in a neutral borate solution at 60 ℃, and then the potential of specimens was kept at this value to examine the change in the structure of anodic oxide films during potentiostatic anodizing. During potentiostatic polarization, specimens-1) and 2) showed the growth of a porous oxide layer on a dense inner oxide layer, whereas specimen-3) showed no appreciable change in the film structure. Impedance measurements on the specimen-3) showed 50 % decrease in the parallel equivalent capacitance after 3 h of potentiostatic anodizing, suggesting a repairing of imperfections in the oxide film.

(8) Structural change in anodic oxide films on aluminum during periodic potential change.

Aluminum specimens covered with amorphous and crystalline anodic oxide films were polarized periodically between a positive potential, E_1, and zero in a neutral borate solution. During the periodic polarization, the dissipation factor, tan δ, of both types of anodic oxide films decreased with time, and this was more remarkable in the crystalline oxide film than in the amorphous one.

(9) Interfacial reaction between Nb and $MoSi_2$

The interfacial reaction between Nb and $MoSi_2$ at high temperatures is being investigated. The aims are to clarify the mechanism of the interfacial reaction and to estimate the maximum application temperature of the composite. The reaction layer was consisting of Mo_5Si_3 and Nb_5Si_3 layers, and the reaction path was clarified. The research on the suppression of the interfacial reaction by inserting diffusion barriers such as Ti, SiC, and Al_2O_2 is also in progress.

(10) Sintering of disilicide by a spark plasma sintering method

A spark plasma sintering method is being applied for fabrication of fully dense metal disilicides ($CrSi_2$, $FeSi_2$, $CoSi_2$, VSi_2, $MoSi_2$). The aims are to clarify the mechanism of the spark plasma sintering and to fabricate disilicides having outstanding oxidation resistance. Sintering in all disilicides starts at almost identical temperature. This suggests that spark occurrs between particles in the initial stage of sintering. All of the disilicides showed outstanding oxidation resistance at 1273 K.

(11) Accelerated oxidation of $MoSi_2$

In order to clarify the mechanism of accelerated oxidation and pesting in $MoSi_2$, low temperature oxidation behavior is being investigated. Simultaneous oxidation of Mo and Si, namely accelerated oxidation, and pesting are liable to occurr in a temperature ranging from 673 to 773 K and preferetially at defects such as pores and cracks. In addition, H_2O vapor in air accelerates the occurrence of pesting. As a result, the accelerated oxidation and pesting are hindered by using fully dense $MoSi_2$.

(12) High temperature oxidation of steels in atmospheres containing H_2O

In order to clarify the effects of H_2O vapor and carbon on the oxidation behavior of steels in a hot rolling process, oxidation tests of iron and steels at 1473 K in a (N_2-3%O_2)-H_2O atmosphere are being done. Formation of many small pores by the reaction of carbon with oxygen and/or FeO was observed in the scale. On the other hand, formation of large pores was suppressed by the addition of H_2O vapor into the N_2-3%O_2 atmosphere.

Other activities

Prof. Takahashi traveled three European countries on March 15 - 22 as a member of delegates from Fac. of Engr., Hokkaido Univ., and visited Technical University of Berlin, Royal Institute of Technology in Stockholm, and University of Cambridge to investigate the education system at the engineering department for undergraduate student. Fortunately, he could meet Profs. C. Leygraf and G. Hultquist at Stockholm and renew his old friendship with them. Prof. Takahashi attended 193rd Meeting of Electrochem. Soc. and presented a paper entitled " Formation of Al-Ti Composite Oxide Films on Aluminum by MOCVD / Anodizing". On September 13-18, ISE Annual Meeting was held in Kitakyushu, and Prof. Takahashi and Mrs. Chu attended it to present papers entitled " Formation of Anodic Oxide Films on Aluminum in Diluted KOH Solutions at Ultra High Potential" and "Localized Deposition of Ni-P alloy on Aluminum by Laser Irradiation and Electroless-Plating". They had pleasant time with Prof. W. Smyrl and his wife, and also Prof. Schlutz and his colleague.

Assoc. Prof. Kurokawa visited Prof. D. J. Young at the Univ. of New South Wales in Australia on 26-30 of Jan., Prof. W. L. Worrell at Univ. of Pennsylvania in U. S. A. on 15 of March to 15 of April, Dr. M. Graham at NRC in Canada on 15-22 of April, and Dr. Schutze at DECHEMA in Germany on 23-26 of April, to discuss the oxidation behavior of $MoSi_2$-based materials. He attended the High Temperature Structural Silicides Conference, which was held at Hyannis in U. S. A. on 26-29 of May, and presented a paper entitled "Low Temperature Oxidation of Fully Dense and Porous $MoSi_2$". After the conference he visited Prof. B. Gleeson at Iowa State Univ. in U. S. A. to discuss the low temperature oxidation of $MoSi_2$. Assoc. Prof. Kurokawa also attended the 6th Conference of Univ. of Sci. and Tech. Beijing and Hokkaido Univ., which was held at Beijing in Chaina on 14-16 of Sep., and presented a paper entitled "Synthesis of $MoSi_2$-SiC Composites by a Spark Plasma Sintering Method".

Foreign researchers visiting the IMSA- Laboratory are Prof. W. L. Worrell at Univ. of Pennsylvania in U. S. A. on 8-10 of Sep, Dr. P. Schmuki and Dr. S. Virtanen, Swiss Federal Institute of Technology, Switzerland on 29 of November - 2 of December.

Presentations

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Role of Surface and Interface Control in High Temperature Materials; K. Kurokawa: The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, July, 1998.

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Effects of Anions on the Reformation of Anodic Oxide Films after Destruction by Laser Irradiation; Y. Ohira, M. Sakairi, and H. Takahashi: ibid.

Formation of Al-Zr Composite Oxide Films on Aluminum by Sol-Gel Coating and Anodizing; H. Takahashi, K. Watanabe, M. Sakairi, S. Hirai, and S. Yamaguchi: Intern. Symp. on Electrochem. of Ordered Interfaces, Sapporo, Sept., 1998.

Formation of Anodic Oxide films on Aluminum in Diluted KOH Solutions at Ultra High Potential; H. Shimada, M. Sakairi, and H. Takahashi: 49th Annual Meeting of ISE, Kitakyushu, Sept., 1998.

Localized Deposition of Ni-P Alloy on Aluminum by Laser Irradiation and

Electroless-Plating; S. Chu, M. Sakairi, and H. Takahashi: 49th Annual Meeting of ISE, Kitakyushu, Sept., 1998.

Synthesis of $MoSi_2$-SiC Composites by a Spark Plasma Sintering Method; K. Kurokawa: The 6th Joint Conference of Univ. of Sci. and Tech. Beijing and Hokkaido Univ., Beijing, China, Sep., 1998.

Effects of Diffusion Barriers on Interfacial Reaction between Nb and $MoSi_2$; G. Ochiai, K. Kurokawa and H. Takahashi: The 123rd Annual Meeting of Jpn. Inst. Metals, Matsuyama, Sep., 1998.

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The research activities cover (1)the development, evaluation and application of dental and biomaterials, (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 microanalysis. Many researches are related to dental, biological and engineering fields and performed in collaboration with clinical departments including prosthodontics, operative dentistry, orthodontics and oral surgery.

Current topics on research are as follows;

(1) 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.

(2) 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 250°C or photopolymerization method. Biocompatible $CaO-P_2O_5-SiO_2-Al_2O_3$ (CPSA) glass fibers of 8-20mm in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bis-GMA. The improvement has been done to obtain the adequate flexural strength and higher torque. FRP wire shows the sufficient flexural strength and a very good elastic recovery. The dependence of Young's modulus and flexural stress on fiber fraction obeys very well the rule of mixture. This FRP wire can cover the range of the strength corresponding to the conventional metal orthodontic wires from Ni-Ti used in the initial stage of orthodontic treatments to Co-Cr used in the last stage by changing the volume ratio of glass fibers with the same external diameter. FRP wire can satisfy both mechanical properties and estheticity, which is not possible for the conventional metal wire.

(3) 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.

(4) 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.

(5) Dental Applications of Acoustic Emission Technique

fracture toughness of dental materials including more detailed discussions using an acoustic emission technique. Acoustic emission (AE) is employed to evaluate the microscopic and macroscopic aspects of mechanical behavior of metal-,ceramics- and polymers- based materials and their composite materials.

(6) Grafting of Methyl Methacrylate onto Collagen Using Ferric Chloride-N-Phenylglycine

Graft polymerization of vinyl monomer onto human hard tissues has not been studied extensively, without tri-n-buthylborane initiated MMA-based materials.The purpose of this study was to grafting of MMA onto collagen using various ferric ions-N-phenylglycine as a redox initiator.

(7) Development of halide fluxes for titanium soldering

The reactivity of KHF_2-LiF-NaCl-KCl fluxes with titanium were examined. The reactivity of the fluxes were promoted in the order of (NaCl+KCl)<(56KHF_2-14LiF-30(NaCl+KCl))<(50KHF_2-50LiF)<(70KHF_2-30LiF)<(KHF_2)<LiF.The reactivity of the fluxes was not alway consistent with the increasing in the spreading areas of solder.

(8) 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.

(9) 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.

Other activities:

The collaboration with Division of High Temperature Materials Science of Institute for Materials Research, Tohoku University (Prof.Toshio HIRAI, Dr.Mamoru OMORI) on the fabrication of new biomaterials including composite materials and functionally graded materials by applying a spark plasma system(SPS) as a method to enhance sintering is undergoing. The research on the surface treatment of Ti by sol-gel method and evaluation of cytotoxicity is developed in cooperation with Department of Materials Science and Engineering, Muroran Institute of Technology(Prof.Kazuyoshi SHIMAKAGE, Assoc.Prof.Shinji HIRAI).

The collaborations are also continued with Institute of Dental Materials Science, Umeå University, SWEDEN (Emerita Prof. Maud BERGMAN, Prof.Lars-Åke LINDÈN) on application of Ti, ZrO_2 for dentistry, research on side effects and other subjects, and with Department of Dental Materials, Chonbuk National University, KOREA (Prof.Tae-Sung BAE) on evaluation of mechanical properties of Ti, dental porcelain and other subjects.

Prof.Tae-Sung BAE of Department of Dental Materials, Chonbuk National University (KOREA), which is a sister school with Hokkaido University School of Dentistry, stayed for June 23-August 23 under the subject of "Investigation on the effect of surface treatment of titanium on precipitation of calcium phosphate" and made a presentation on "Propagation of micro cracks in dental ceramics".

Presentations

Biocompatibility and bioreactivity of Ti-based functionally graded implant; F.Watari, A.Yokoyama, F.Saso, H.Matsuno, M.Uo, T.Kawasaki: 9th CIMTEC(Int.Conf.on Modern Materials & Technologies/World Ceramic Congress & Forum on New Materials), Florence(Italy), June, 1998

Biocompatibility of Titanium/hydroxyapatite and Titanium/Cobalt Functionally Graded Implants; F.Watari, A.Yokoyama, F.Saso, H.Matsuno, M.Uo, T.Kawasaki: 5th Int.Symp.on Functionally Graded Materials, Dresden, Oct., 1998

Fracture Tougheness of Expansible Microshere-Filled Denture Base Resin; S.Kondo, S.Ohkawa, M.Uo, T.Sugawara and F.Watari: The 77th International Association for Dental Research., Nice, France, June, 1998.

Effect of Heating Times in Joint Strengths of Titanium; S.Ohkawa, S.Kondo, M.Uo, T.Sugawara and F.Watari: The 77th International Association for Dental Research., Nice, France, June, 1998.

Effects on mechanical properties of new FRP orthodontic wire under water immersion; T.Imai, S.Yamagata, F.Watari, M.Kobayashi, T.Yamamoto, K.Umeda, S.Nakamura: The 77th International Association for Dental Research., Nice, France, June, 1998.

Study on the fabrication and biocompatibility of titanium/hydroxyapatite functionally graded implant; F.Saso, H.Matsuno, A.Yokoyama, M.Uo, F.Watari, T.Kawasaki: The 77th International Association for Dental Research., Nice, France, June, 1998.

Simplified fabrication method of porcelain inlay using cold isostatic press; C.Kawamoto, F.Watari, M.Uo, H.Komatsu and H.Sano: The 77th International Association for Dental Research., Nice, France, June, 1998.

Effect of Powder Constituents on Fracture Toughness of Acrylic Denture Base Resin; S.Kondo, S.Ohkawa, M.Uo, T.Sugawara and F.Watari: The 31th Jap.Dent.Mater.and Dev.,Yokohama, Apr.,1998.

Study on Biocompatibility of Refractory Metals Ti, Nb, Hf, Ta, Re; H,Matsuno, F.Saso, A.Yokoyama, T.Kawasaki, M.Uo, T.Sugawara, S.Kondo, S.Ohkawa and F.Watari: The 31th Jap.Dent.Mater.and Dev.,Yokohama, Apr.,1998.

An Experimental Study about the Surface Treatment of the esthetic Orthodontic Wire; K.Nagayama, S.Yamagata, H.Toyoizumi, T.Imai, S.Nakamura, S.Kondo, S.Ohkawa, M.Uo, T.Sugawara. F.Watari: The 31th Jap.Dent.Mater.and Dev.,Yokohama, Apr.,1998.

Mechanical Properties of Esthetic Orthodontic Wires in Torsion; H.Toyoizumi, S.Yamagata, K.Nagayama, T.Imai, S.Nakamura, S.Kondo, S.Ohkawa, M.Uo, T.Sugawara. F.Watari: The 31th Jap.Dent.Mater.and Dev.,Yokohama, Apr.,1998.

Flexural Properties of Solid and Hollw Microsphere Filled Denture Base Resins; S.Kondo, S.Ohkawa, M.Uo, T.Sugawara and F.Watari: The 32th Jap. Dent.Mater.and Dev.,Niigata, Oct.,1998.

Observation of Metal Implanted Soft Tissues with X-ray Scanning Analytical Microscope; M.Uo, T.Sugawara, S.Kondo, S.Ohkawa, F.Watari, H,Matsuno, A.Yokoyama and T.Kawasaki: The 32th Jap.Dent.Mater.and Dev.,Niigata, Oct.,1998.

Observation of the Newly Formed Bone Around High Melting Temperature Metal Implants; H,Matsuno, F.Saso, A.Yokoyama, T.Kawasaki, M.Uo, T.Sugawara, S.Kondo, S.Ohkawa and F.Watari: The 32th Jap.Dent.Mater.and Dev.,Niigata, Oct.,1998.

Tissue Response to Ti/HAP Functionally Graded Materials Inserted in Rabbit Tibia; F.Saso, H.Matsuno,A.Yokoyama, T.Kawasaki, M.Uo, T.Sugawara, S.Kondo, S.Ohkawa and F.Watari: The 32th Jap.Dent.Mater.and Dev.,Niigata, Oct.,1998.

Coating procedure on the surface of the esthetic orthodontic wire; K.Nagayama, S.Yamagata, H.Toyoizumi, T.Imai, S.Nakamura, F.Watari and M.Kobayashi: The 46th JADR, Chiba, Nov., 1998

Observation of Biocompatibility and Biohazardness of Metallic Implants; F.Watari, A.Yokoyama, M.Uo, H.Matsuno, F.Saso, T.Kawasaki: The 123th Annual Meeting of Jpn.Inst.Metals.,Matsuyama,Sept.,1998

Recent Cases of Localized "Ant's Nest" Corrosion in Copper Tubes

Takenori Notoya and Kozo Kawano

J. Japan Copper and Brass Research Association, **37**, 27-33 (1998)

The localized "Ant's nest" corrosion in copper tubes, which are widely used in refrigerating and air-conditioning units, has been detected during the early stage of service and in leakage tests conducted after manufacturing. The morphology of this corrosion is similar to ant's nest when viewed in cross section. The optical microscopic examination of cross sections show corroded parts with an underlying labyrinth of interconnecting channels containing copper oxide in random micropaths. This type of corrosion is caused by the decomposition products from chlorinated organic solvents used to degrease the tubes and from some types of lubricant oil used during the copper tubing stamping process. More recently, volatile organic substances from vinegar-containing seasonings, adhesives from synthetic building materials, cosmetics and perfumes, woods, and insecticides are also suspected as corrosive agents. These decomposition products and volatile organic substances include carboxylic acids, aldehydes and alcohols. In spite of extensive studies and recommendations, the ant's nest corrosion in copper tube is still found in approximately 10 % of total premature failures of copper tubes in Japan. In thispaper, recent five cases of ant's nest corrosion in copper tubes, corrosion mechanisms and its preventive measures are presented. (Japanese)

Copper and Evolution

Takenori Notoya

Copper and Brass, No.146, p.12 (1998)

Copper is one of the essential metallic nutriments for living creatures on the earth. This short essay describes the importance of a trace amount of copper for living things in the sea and human being, and explains the reasons. (Japanese)

Comparative Investigation of Several Corrosion Inhibitors of Copper by Using AC Impedance Spectroscopy

Xu Qunjie, Zhou Guoding, Lu Zhu and Takenori Notoya

Journal of East China University of Science and Technology **24**, No.3,
324-328 (1998)

The corrosion inhibition of copper electrode in sodium chloride solutions of pH 6 with various inhibitors such as benzotriazole (BTA), tolyltriazole (TTA) , 5-methylbenzotriazole (5MBTA) and carboxybenzotriazole methyl ester (CBTME) was studied by using AC impedance spectroscopies. The corrosion inhibition of these four inhibitors increases with its concentration up to 70 mg/l. At the low concentrations below 20 mg/l, BTA, TTA and 5MBTA have better inhibition than CBTME and CBTME is the best among them at the concentration over 40 mg/l . A combination of BTA and 5MBTA gives a synergistic effect and the optimum ratio with the total amount of 40 mg/l is 20 mg/l BTA plus 20 mg/l 5MBTA. (Chinese)

Comparative Investigation of Benzotriazole Derivatives for Copper at Different pHs by Using AC Impedance Spectroscopy

Xu Qun-ji, Zhou Guo-Ding, Lu Zhu and Takenori Notoya

proc.corrosion and protection of marine meterials p.266-268 (1998)

The corrosion inhibition of copper electrode in 3% NaCl solutions of three different pHs with various inhibitors such as 4-carboxybenzotriazole (4CBTA), 5-carboxybenzotriazole (5CBTA), 1-carboxybenzotriazole (CBT-1) and benzotriazole (BTA) was studied by using ac impedance spectroscopies. The results show that 4CBTA, 5CBTA, CBT-1 have better inhibition for copper at pH = 3 than BTA. THe 4CBTA has best inhibition effect among the four inhibitors. Hoewver,at pH = 6 and 9 they don'tshow any inhibition for copper except BTA. (Chinese)

The Influence of the Growth Rate of the Semiconductive Properties of Titanium Anodic Oxide Film

Toshiaki Ohtsuka and Tetsuo Otsuki

Corros. Sci., **40** (6), 951-958 (1998)

The semiconductive properties of the anodic oxide films on titanium formed by potential sweep oxidation at various sweep rates is investigated by AC impedance in 0.1 mol dm^{-3} sulfuric acid solution. The dielectric constant and donor density of the oxide films change with the sweep rate. The dielectric constant increases and the donor density decreases with increase of the sweep rate. The dependence may be interpreted by the degree of hydration of the film. The oxide film formed by the higher sweep rate is more hydrated. High content of the hydrating water or an OH^- bridge in the film may introduce a relatively high dielectric constant and low donor density. (English)

Effect of Ferrous Ion in Solution on the Formation of Anodic Oxide Film on Iron

Toshiaki Ohtsuka and Hirotaka Yamada

Corros. Sci., **40** (7), 1131-1138 (1998)

The effect of Fe^{2+} ion in the solution on the anodic formation of the passive oxide film onto iron was investigated by the ellipsometric trace of the film growth in a borate solution at pH 8.4. In addition to a compact inner passive layer, formed by initial direct oxidation, the Fe^{2+} ion in the solution is oxidized to build up an outer hydrous layer at the latter stage. The inner layer behaves similarly as the usual passive film, in which the film growth follows the ionic migration mechanism under high electric field. The outer layer growth may, however, be determined by a surface reaction between the film and the electrolyte solution, i. e., the growth rate is independent of potential and a linear function of the Fe^{2+} ion concentration in the solution. (English)

Structure of Anodic Oxide Films on Titanium

Toshiaki Ohtsuka

Hyomen Kagaku (Surface Science of Japan), **19** (12), 799-804 (1998)

Recent studies of the anodic oxide films on titanium are reviewed. In-situ electrochemical techniques including AC impedance, optical reflection like ellipsometry, photoelectrochemistry, and Raman spectroscopy have been used.

The results are summarized as follows: (1) The TiO_2 film is amorphous at potentials lower than 5 V but changes to anatase type at potentials higher than 5 V. (2) Thickness of the film is linearly proportional to the anodic potential on the potential range lower than 7 V. However, the ratio of the thickness to potential becomes larger if the potential is higher tan 7 V probably due to formation of an ionic leakage path accompanied by crystallization of the film. (3) The film behaves as an n-type semiconductive electrode with a high concentration of donor density and bandgap of 3.2 eV. (Japanese)

Changes in Luminescence Poperties of Porous Silicon Layer due to Anodic Oxidation

Kazuhiro Shigyo, Kazuhisa Azumi and Masahiro Seo

DENKI KAGAKU (Presently Electrochemistry), **66**, 92 - 99 (1998)

A porous silicon layer (PSL) was prepared on p-type single crystal Si (100) wafer with an electrochemical etching in ethanol solution of 22.6.wt % HF. An anodic oxidation of PSL until 500 V (SHE) in 0.1 M KNO_3 ethylene glycol solution was performed to improve visible photoluminescence (PL) properties of PSL. Moreover, an electroluminescence (EL) emitted from PSL during anodic oxidation was measured to understand anodic oxidation mechanism of PSL. THe TEM images and FTIR spectra have indicated that PSL as prepared consists of Si nanoparticles with a diameter of 2 nm - 5 nm and the Si nanoparticles are covered with silicon hydrides, SiH_x.

At the initial stage of anodic oxidation of PSL where the potential remains a low value, silicon hydrides on Si nanoparticles are firstly oxidized and simultaneously an EL with a peak wavelength of 800 nm - 710 nm is emitted from the PSL. In the subsequent oxidation region where the potential rises linearly with time, Si nanoparticles are oxidized to SiO_2 and simultaneously an EL with two peak wavelength of 650 nm and 530 nm is emitted from the PSL. The origins of these EL emission sources were explained by using an electronic band model of Si/SiH_x/solution interfaces or Si/SiO_2/solution interfaces.

The PL spectra of PSL as prepared have a peak wavelength of 660 nm. The PL intensity increases and the PL spectra shifts toward short wavelength as anodic oxidation of PSL proceeds. It has been discussed by using the electronic band model that the decrease in surface state density of Si nanoparticles due to anodic oxidation would enhance significantly the PL intensity. The above results support that the quantum confinement effect is operative in the visible PL of PSL subjected to anodic oxidation. (Japanese)

Structure and Properties of Anodic Oxide Film on Titanium

K. Azumi

The Journal of the Surface Finishing Society of Japan, **49**, 39-43 (1998)

Structure, properties, and applications of the anodic oxide film formed on titanium were reviewed. Relationship between oxide film thickening and crystallization with increase of anodic oxidation potential was shown with AFM images. High-corrosion resistivity, photo-catalytic property, electrochromic and interference chromic properties were explained concerning with the n-type semiconductive properties of the oxide film. (Japanese)

Formation of Al-Ti Composite Oxide Films On Aluminum By MOCVD/Anodizing

H. Takahashi, H. Kamada, M. Sakairi,
K. Takahiro*, S. Nagata*, and S. Yamaguchi*

Proc. Intern. Symp. on Dielectric Material Integration for Microelectronics,
p. 253-262 (1998)

Al-Ti composite anodic oxide films were formed on aluminum by anodizing in a neutral borate solution after coating of TiO_2 with MOCVD to examine their structure and dielectric properties. During galvanostatic anodizing, anodic oxide films were formed at the interface between TiO_2 layer and the metal substrate, and they consisted of two layers: an inner pure alumina layer and an outer Al-Ti composite oxide layer. The thickness of both layers increased with anode potential, E_a, and the thickness ratio of the outer layer against inner layer was larger at higher specimen temperatures during MOCVD. The heat treatment of specimen before anodizing caused the formation of a crystalline oxide layer and the parallel capacitance of the anodic oxide film formed by MOCVD/heating /anodizing was 60 % higher than that formed on elctropolished specimen. (English)

Study of Initial Layer Formation of Zn-Ni Alloy Electrodeposition by In Situ Ellipsometry

Toshiaki Ohtsuka and Akira Komori

Electrochim. Acta, **43** (21-22), 3269-3276 (1998)

Initial layer of Zn, Ni, and Zn-Ni alloy electrodeposition on Au electrode in sulfate baths are detected in a nm thickness range by in- situ ellipsometry. The thin layer deposits are also analyzed by Auger electron spectroscopy (AES) and ICP atomic emission spectroscopy. The preferential deposition of Zn, in the initial thin layer of Zn-Ni alloy deposition, is confirmed by the analysis. From the ellipsometric measurements, the underpotential deposition (UPD) of Zn is observed; i. e. the Zn deposition starts at a potential more positive by 0.5 V than the redox potential of Zn^{2+}/Zn, while noticeable UPD of Ni cannot be observed. For Zn-Ni alloy deposition, the thin layer of Zn formed in the UPD potential region greatly inhibits the Ni deposition. It is speculated that the preferential Zn deposition in Zn-Ni alloy electroplating is caused by the inhibition of Ni nuclei growth due to a thin layer of Zn on the deposited Zn-Ni alloy. (English)

Water Layer on Gold as Investigated by in situ Simultaneous Measurement with IR-RAS and QCM

T. Sasaki, J. Itoh, M. Seo and T. Ishikawa,

Proc. ECS, **97-26**, 100-107 (1997)

To investigate the behavior of water on a gold surface in humid nitrogen, in situ simultaneous measurements with IR-RAS and QCM were carried out. IR spectra of adsorbed water layers of various thicknesses, which were prepared in nitrogen with controlled relative humidity, were successfully measured .

The shapes and intensities of IR-RAS spectra of water were compared with those of bulk water. Thin layer of adsorbed water showed very different shapes and intensities of IR band of bending mode from those of bulk water, and they became similar to those of bulk water with increase in thickness. (English)

Measurement of Membrane Potentials of PbO_2 and $PbSO_4$ Prepared with Electrosynthesis

Miki Ushito and Masahiro Seo

DENKI KAGAKU (Presently Electrochemistry), **66**, 398-404 (1998)

PbO_2 was electrochemically deposited on a Pt mesh in $Pb(NO_3)_2$ /HNO_3 aqueous solution and subsequently electrochemically converted to $PbSO_4$ in H_2SO_4. The Pb compounds were identified with β-PbO_2 and $PbSO_4$, respectively, by using a thin film X-ray diffraction method (XRD). The surface morphology of β-PbO_2 and $PbSO_4$ were observed with a scanning electron microscope (SEM). The ion-selective properties of β-PbO_2 and $PbSO_4$ were investigated by measuring the membrane potential as a function of electrolyte concentration in various electrolyte solutions.

In neutral solutions such as NaCl, KCl and Na_2SO_4, β-PbO_2 was cation-selective, whereas $PbSO_4$ was anion-selective. In H_2SO_4 solution, however, both membranes were cation-selective. The roles of these ion-selective properties in discharge-charge reaction of a lead-acid battery were discussed. (Japanese)

Corrosion Kinetics of Iron Thin Film in Dearated Phosphate Solutions by an Electrochemical Quartz Crystal Microbalance

Masahiro Seo and Masato Kurosaki

ECS Proceedings Volume, **97-26**, 221-230 (1998)

The corrosion rates of iron thin film in deaerated phosphate solutions were measured by an electrochemical quartz crystal microbalance as a function of solution pH or phosphorus concentration in solutions. The dependences of corrosion rate and corrosion potential on solution pH and phosphorus concentration have suggested that the corrosion mechanism changes in the vicinity of pH 5 and $H_2PO_4^-$ contributes more significantly to the corrosion processes of iron at pH 6.5 than at pH 3.0. (English)

CRGHU

Piezoelectric Detection of Changes in Surface Energy of an Iron Electrode

Kaoru Ueno and Masahiro Seo

ECS Proceedings Volume, **97-26**, 275-284 (1998)

A piezoelectric technique was applied to an iron electrode to investigate adsorption of electrolyte anions (ClO_4^-, SO_4^{2-}, Cl^-, Br^- and I^-) which would play important roles in the corrosion mechanism and stability of passive film on iron. The potential of zero charge (pzc) of iron in the hydrogen evolution / active dissolution region could be evaluated from the piezoelectric signal curve. It has been found that pzc of iron shifts to the negative direction in the order of $Cl^- = Br^- = I^- > SO_4^{2-} > ClO_4^-$. The order of negative shift in pzc of iron was different from that of mercury or noble metals such as platinum and gold. This discrepancies were discussed from the view-point of formation of iron electrolyte complex ions which would act as an adsorbed intermediate for iron dissolution or hydrogen evolution reaction.

Moreover, the piezoelectric signal of iron electrode covered with passive film has suggested that adsorption of SO_4^{2-} on passive film increases the surface charge density of passive film, i.e., potential difference at the passive film | solution interface. (English)

Comparative Study between Bromine and Iodine Adlayers on a Polycrystalline Gold Electrode by a Piezoelectric Technique

Kaoru Ueno and Masahiro Seo

DENKI KAGAKU (Presently Electrochemistry), **66**, 713-719 (1998)

The specific adsorption of bromide ions on a polycrystalline gold electrode was investigated by a piezoelectric technique and was compared with that of iodide ions previously reported. The potential of electrocapillary maximum or potential of zero charge (pzc) of the gold electrode could be evaluated from the piezoelectric signal curve.

The iodide and bromide concentration dependencies of pzc have indicated that the adsorption order is $I^- > Br^-$. The another characteristic potential, E_2 at which a sign-reversal of surface charge density seems to take place, appeared in the potential region where the ordered structure of bromine or iodine adlayer on a single crystal gold was stably observed with STM and SXS. The possible model for the sign-reversal of surface charge density at E_2 was proposed, assuming the structural change or phase change of adlayer followed by the ordered structure formation. (English)

Characterization of Anodic Oxide Film Formed on TiN Coating in Neutral Borate Buffer Solution

K. Azumi, S. Watanabe, M. Seo, I. Saeki, Y. Inokuchi, P. James and W. H. Smyrl

Corrosion Science, **40**, 1363-1377 (1998)

Properties of the oxide layer formed on a TiN coating by anodic oxidation in neutral borate buffer solution were investigated using cyclic voltammetry, AFM, FT-IR, impedance and photocurrent measurements. The voltammogram showed imperfections in the TiN coating and high susceptibility of anodic oxidation. The result of FT-IR showed the composition of an oxide layer, similar to TiO_2, including OH^- or water. Both impedance and photocurrent results confirmed that the oxide film has n-type semiconductor properties. The oxide would contain defects acting as intergap states, resulting in low efficiency of photo-induced free-carrier generation. It seems that these defects have their origin in degradation of the protective property of a TiN coating under anodic polarization. (English)

Evaluation of the Heterogeneity of Corroding Surface by Scanning Electrochemical Microscopy

Masahiro Seo and Koji Fushimi

Corrsion Division, Soc. Materials Sci. Jpn. Report, **37**, 40-50 (1998)

A scanning electrochemical microscope (SECM) is powerful and useful technique for evaluation of heterogeneity of electrochemical reaction which takes place on electrode surface. In this article, the principle and measurement mode of SECM were explained and the results of application of SECM to the passive films on iron and titanium were described. The redox reaction of $Fe(CN)_6^{3-}$ / $Fe(CN)_6^{4-}$ was employed asa mediater to evaluate the difference in electrochemical reactivity on the local area of passive films.

The probe current image could detect the difference in thickness of passive film formed on iron in pH 8.4 borate soultion. Moreover, the micropatterns of the probe current image coincided with the photomicrograph of passivated iron surface and indicated that the thickness of passive film depended on the orientaion of the substrate iron grains. The probe current image also indicated that the heterogeneity of passive film on titanium in pH 8.4 borate solution increased with increasing the film formation potential and the thickness of passive film depended on the substrate grains. (Japanese)

Electrochemical Method for Atmospheric Corrosion- Electrochemical Measurement under Thin Electrolyte Solution
(3) EQCM

Masahiro Seo

DENKI KAGAKU (Presently Electrochemistry), **66**, 504-509 (1998)

This article dealt with application of electrochemical quartz crystal microbalance (EQCM) to atmospheric corrosion of metal thin film under thin electrolyte solution. After the principle of EQCM was explained briefly, the EQCM results of aqueous corrosion of iron thin film in phosphate solutions were described as a typical example and the corrosion mechanism was discussed from the dependence of mass loss rate of the iron thin film on solution pH or phosphate concentration.

Moreover, it has been pointed out that the mass change converted from the resonant frequency change of quartz oscillator produces some errors when the density and visicosity of thin electrolyte solution change significantly due to the the enrichment of dissolved metal ions in solution side near the metal / solution. interface. (Japanese)

Characterization and Structural Observation of Ag-ion Diffused Glasses by Scanning Acoustic Microscopy

Kemas Zaini THOSIN, Isao ISHIKAWA and Toshio NARITA

Hihakai-Kensa, **47**, 253-258 (1998)

Acoustic micro-spectroscopy was utilized to observe and characterize Ag-ion and Ag-colloid glasses using various frequencies between 75 and 450 MHz. Scanning acoustic micrographs showed that the Ag-ion glass has a homogeneous structure, while the Ag-colloid glass became heterogeneous with white spots from voids when a frequency of 400 MHz was used. A leaky surface acoustic wave (LSAW) was observed over the whole frequency range, and its velocity decreased with increasing frequency, while a leaky skimming surface compressional wave(LSSCW) appeared at frequencies higher than 300 MHz. Compressional stress was estimated from changes in LSAW velocities among the Ag-ion and Ag-colloid glass layers as well as a glass containing Ag-ion. (Japanese)

Characteristics of K_2TiCl_6 Synthesis from KCl and $TiCl_4$

Takehiko Kumagai, Shoichi Konda, Takeshi Sasaki, Tatsuo Ishikawa and
Tadatoshi Chiba

Kagaku Kogaku Ronbunshu, **24**, 558-561 (1998)

Reaction characteristics were examined for synthesis of K_2TiCl_6 from KCl particles and $TiCl_4$ gas. The reaction experiments were carried out exposing different sizes of KCl particles to a $TiCl_4$ gas stream at 683 K. The mass gain due to formation of K_2TiCl_6 was measured as a function of time and morphology of the product was observed by SEM and EPMA. The apparent reaction rate decreases rapidly with the progress of the reaction, and the reaction is virtually terminated before its completion EPMA analysis on the particle cross-section reveals that the products are distributed around an unreacted KCl core within the particle, and the termination of the reaction takes place when the thickness of the outer product layer grows up to about 6mm. The reaction kinetics are explained well on the basis of an unreacted-core model which assumes that the rate determining step is the intra-particle $TiCl_4$ gas diffusion. (Japanese)

Abstracts of Publications

Characteristics of $TiCl_4$ Dissolution into Equimolar NaCl-KCl Molten Salt

Takehiko Kumagai, Shoichi Konda, Takeshi Sasaki and Tatsuo Ishikawa

DENKI KAGAKU (Presently Electrochemistry), **66**, 55-60 (1998)

The maximum concentration of $TiCl_4$ in equimolar NaCl-KCl molten salt was experimentally determined at 750°C and 1 bar. In the experiment, a salt sample with a $TiCl_4$ concentration, $C_{Ti}{}^0$, of 16.5 mol% was prepared from a mixture of K_2TiCl_6 powder, NaCl and KCl. The sample was heated up to 750°C and melted under the $TiCl_4$ atmosphere in a closed glass ampule. The concentration of Ti in the sample was measured by ICP spectroscopy and was found to be larger than 10 mol% of $TiCl_4$ due to increased pressure upon heating. The sample was then heated at 750°C for 5min under the 1 bar $TiCl_4$ gas atmosphere and cooled rapidly in a water bath. The concentration, C_{Ti}, was measured for Ti finally left in the sample. The measurements were carried out for samples with different $C_{Ti}{}^0$'s. It was found that C_{Ti} gradually increases with $C_{Ti}{}^0$ and levels off at $C_{Ti}{}^0$ being approximately 13 mol%. The equilibrium solubility was determined as 6.5 ± 0.5 mol% at 750°C and 1 bar. A mixture containing 5.5 mol% $TiCl_4$ was prepared from K_2TiCl_6, KCl and NaCl. The mixture was fused in an open vessel at 750°C and 1 bar. The concentration of $TiCl_4$ finally left in the melts was 2.9 mol%. (Japanese)

Electrorefining of Aluminum in $BaCl_2$-NaCl Melts Containing AlF_3-NaF

Mikito UEDA, Shoichi KONDA, Takeshi SASAKI and Tatsuo ISHIKAWA

DENKI KAGAKU (Presently Electrochemistry), **66**, 164-170 (1998)

Anodic dissolution behavior of several aluminum alloys containing Fe (1 ~ 3 mass %), Si (0.2 ~ 3 mass %) and Mg (0.3 mass %) was investigated in molten salts predominantly composed of chloride, which were developed for electrorefining of aluminum from aluminum scraps in a three-layer cell. During 12 hour electrolysis using the aluminum alloys, the aluminum content in the melts, 5 mol % AlF_3-NaF-$BaCl_2$-NaCl, was kept constant and the overvoltage of both anodic and cathodic reactions was negligible small. It suggested that the melts were applicable to the system for Al electrorefining.

The analysis of the melts and the deposited Al every three hours showed that Fe content in the deposited Al was less than 0.01 mass % and that of Mg was negligibly small, and the contents of Si became about one thirtieth of the starting anode alloys. The Fe content up to 3 mass % in anode alloys brought about no significant problems. (Japanese)

Electrorefining of Aluminum Containing 1mass% Fe Using a Bipolar Electrode Cell

Mikito UEDA, Shoichi KONDA, Takeshi SASAKI and Tatsuo ISHIKAWA

Electrochemical Society proceedings volume, **98-11**, 363-369 (1998)

To investigate the applicability of a vertically stacked bipolar electrode cell to electrorefining of Al from scrap Al, the cell composed of three units was made with anode 61%Al - 37.3%Cu alloy containing 1%Fe and 0.7% Mn (mass) in melt and electrolysis was carried out for six hours at 750 °C.

As the electricity of 90 Ahr, which corresponded to Al deposition of 30.0g per cathode in 100% current efficiency, was applied, the total mass of electrodeposited Al was 87.5g. The amounts of Mn, Cu and Fe in deposited Al were under 0.003, 0.008 and 0.009 %, respectively; the purity of Al exceeded 99.98%. The concentration of Al components in the 3rd unit containing a terminal anode increased compared with the initial concentration, and that in the 1st unit containing a terminal cathode decreased. It was interpreted that the reaction current through bipolar electrodes became small due to bypass current, and the bipolar electrodes worked almost ideally. The vertically stacked bipolar electrode cell is, therefore, useful for electrorefining of Al from scrap Al, if some counterpane to dissolve the ununiformity of the concentration in the cell is laid down. (English)

Electrowinning of Liquid Aluminum from Chloride Melts by Using a Bipolar Electrode Cell.
I. Design Principle of a Bipolar Electrode Cell

Shoichi Konda, Takeshi Sasaki, Mikito Ueda and Tatsuo Ishikawa

DENKI KAGAKU (Presently Electrochemistry), **66**, 74-79 (1998)

In order to develop an energy saving process for electrowinning of liquid aluminum from chloride melts, a design principle for a bipolar electrode cell was developed and the design parameters suitable for its operation were determined on the basis of experiments in 25 mol% $MgCl_2$-75 mol% NaCl melts containing several mol% $AlCl_3$ at 750°C. (Japanese)

Electrowinning of Liquid Aluminum from Chloride Melts by Using a Bipolar Electrode Cell

II. Estimation of Characteristics of the Cell under Operation.

Shoichi Konda, Takeshi Sasaki, Mikito Ueda and Tatsuo Ishikawa

DENKI KAGAKU (Presently Electrochemistry), **66**, 80-86 (1998)

The decomposition voltage of aluminum chloride and the electrical conductivity were determined as a function of concentration of aluminum chloride in 25 mol% $MgCl_2$-NaCl melts in order to estimate the characteristics of a bipolar electrode cell. The relations between voltage and applied current were calculated from an equivalent circuit of the bipolar electrode cell of which components were determined by using these properties of the melts and the parameters of the cell design. The calculated relations were in fair agreement with the experimental results. This suggests that the procedure mentioned above makes it possible for us to estimate the characteristics of the cell and select the suitable electrolysis conditions without the operation of the cell. (Japanese)

CRGHU

The Effect of the Oxidation Atmosphere on the Initial Oxidation of Type 430 Stainless Steel at 1273 K

I. Saeki, H. Konno, R. Furuichi, T. Nakamura, K. Mabuchi, and M. Itoh

Corrosion Science, **40**, 191-200 (1998)

Type 430 stainless steel with 0.9 wt% manganese was oxidized in $O_2/H_2O/N_2$ atmospheres at 1273 K. Iron-rich corundum-type oxide formed in the very initial oxidation stage changed to a chromium-rich oxide with time in all atmospheres. The chromium content in a spinel-type oxide, which appeared after formation of the corundum-type oxide, increased with increasing oxygen partial pressure. It is considered that the spinel-type oxide forms through a two-step reaction: first, reduction of Mn_2O_3 to MnO; second, solid-state reaction of MnO with corundum oxide. The rate-determining step appears to be the first reaction. (English)

Growth Process of Protective Oxide Formed on Type 304 and 430 Stainless Steels at 1273 K

I. Saeki, T. Saito, R. Furuichi, H. Konno, T. Nakamura, K. Mabuchi, and M. Itoh

Corrosion Science, **40**, 1295-1302 (1998)

Oxidation of Type 304 and 430 stainless steels for up to 1 h was studied at 1273 K and the composition and structure of the oxide were determined by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). In the initial several tens of seconds, only iron-rich corundum-type oxide was formed, whereas the final oxide was composed of an inner chromium-rich corundum-type oxide layer and an outer mixed layer of corundum-type and spinel-type oxides. An iron-rich metallic α phase was observed on Type 304 stainless steel. This suggests a growth mechanism where corundum-type oxide on Type 304 stainless steel repeats cycles of breakage and curing of the oxide, resulting in the formation of metallic α phase in the oxide layer. A similar reaction is postulated to take place in the oxidation of Type 430 stainless steel. (English)

High Temperature Corrosion Kinetics of Ni-Cr Alloys in HCl-containing Atmosphere

Yoshiyuki Sato Motoi Hara and Toshio Narita

Zairyo-to-Kankyo, **47**, 313-319 (1998)

High temperature corrosion kinetics of Ni-Cr alloys in a 1%HCl–50%O_2–N_2 atmosphere was investigated by thermogravimetric technique. The mass change curves of the specimens showed a slight gain in the initial period and a subsequent linear loss. Since such corrosion behavior was due to the formation of $NiCl_2$ and its vaporization besides the oxide formation, the equation of mass change curve included the terms of mass gain and evaporation curve. However, the conventional kinetics consisting of the terms of a parabolic mass gain curve and a linear evaporation curve did not completely describe the experimental results in the 1%HCl atmosphere. Therefore, in this study, the kinetics equation was introduced on the assumption that the evaporation curve was divided into two curves; one was the curve which represented the rate of chlorination of Ni and the other was the curve which represented the chlorination of NiO. The chlorination of NiO occurred owing to the solving of $NiCl_2$ into the NiO scale. In addition, it was presumed that some incubation periods existed until the vaporization of $NiCl_2$ became significant. The kinetics equation introduced on these assumptions well described the experimental mass change of Ni-Cr alloys very well in the 1%HCl atmosphere. (Japanese)

Effects of Impurity Oxygen and Si Addition on High-Temperature Nitridation of Ti-Al Alloys

Takanori Watanabe, Takayuki Yoshioka and Toshio Narita

Zairyo-to-Kankyo, **47**, 333-340 (1998)

Nitridation behaviour of Ti-50Al, Ti-50Al-3Si, and Ti-47Al-3Si alloys was investigated at 1173 K for up to 518.4 ks in a N_2 gas with 99.9995 purity (less than 0.5 ppmO_2) and the N_2 gases purified with Ti or Ti+ AlN getter, i.e., $N_{2(Ti)}$ and $N_{2(Ti+AlN)}$ gases. Structural sequences of products on a Ti-50Al alloy are nitrides (Ti_2AlN + TiN)-$TiAl_2$ in the $N_{2(Ti+AlN)}$ gas, nitrides(Ti_2AlN + TiN +AlN)-$TiAl_3$-$TiAl_2$ in the N_2(Ti) gas, and oxides(TiO_2 + Al_2O_3)-nitrides(Ti_2AlN+TiN) in an as-received N_2 gas. In cases of TiAl alloys containing Si, oxides(TiO_2+Al_2O_3)-nitrides(Ti_2AlN + TiN+ AlN)-$TiAl_3$-$TiAl_2$ were formed in an as-received N_2 gas, and nitrides(Ti_2AlN+TiN +AlN)-$TiAl_3$-$TiAl_2$ in both the N_2(Ti) and N_2(Ti +AlN) gases. Selective nitridation of Ti yields Al-enriched layers of $TiAl_2$ and $TiAl_3$ on the alloy surface and they could be explained from thermodynamical considerations. A periodic formation of Ti_2AlN+TiN and AlN layers, looks like a Liesegang phenomenon, is due to a competitive process of a rapid N_2 gas ingress and a so-called back-diffusion of Al toward the alloy substrate. A part of a Ti-Al-N ternary phase diagram at 1173 K was given, showing compositional paths for these nitridation reactions. Nitridation rate was very low for a Ti-50Al alloy in the N_2(Ti+AlN) gas, while it tended to increase with time in an as-received gas and the N_2(Ti) gas. TiAl alloys containing Si showed large nitridation rates, accompanied by a catastrophe in nature in each atmosphere. It was suggested that Si addition and impurity oxygen in N_2 gas gave deteriorative effects on nitridation property of Ti-Al alloys at high temperatures. (Japanese)

High Temperature Corrosion Behavior of a Heat Resistant Steel SCH13 in Waste Incinerator Environments

Hidenori Takahashi, Yasuki Miyakoshi, Syuichi Kamota,
Shigenari Hayashi and Toshio Narita

Zairyo-to-Kankyo, **47**, 777-782 (1998)

High temperature corrosion behavior of a SCH13 steel in a waste incineration furnace, where used plastics and tires were burned in the day-after-day operation, was investigated by means of optical microscope and scanning electron microscope, electron probe micro-analysis, and X-ray diffraction analysis. The SCH 13 steel was put at the exit of the furnace, and the temperature of exhaust gases maintained above 1273 K (maximum is 1423K) for 7 ks and then at 1150 K for 17 ks, followed by furnace cooling. Corrosion products in the surface were mainly oxides as Cr_2O_3, Fe_3O_4, $NiMn_2O_4$, and $FeCr_2O_4$. Internal corrosion products with a network structure were composed of Cr-Mn oxide, and at the internal corrosion front SiO_2 and CrS were formed in link with Cr-Fe carbides and σ-phase, which were precipitated in a network structure during the repeated furnace operation. Laboratory tests on sulfidation or oxidation of both as-received and heat-treated SCH13 steels showed that the Cr-Fe carbides and a -phase were preferentially corroded, forming a network structure. It could be concluded that the internal corrosion of the SCH13 steel suffered from the waste incinerator atmosphere is due to selective sulfidation of Cr-Fe carbides and σ-phase in the internal corrosion front, followed by oxidation to form SiO_2 and Cr-Mn oxide. (Japanese)

Effect of Concentration in Al-Si Alloy Bath on Hot-dipped SUS 304 Stainless Steel Coating Layer Formation

Junichi Tanaka, Kenichi Ohsasa and Toshio Narita

The Journal of the Surface Finishing Society of Japan, **49**, 496 - 501 (1998)

SUS 304 stainless steel plate was dipped in molten Al-Si alloy having different Si concentrations, i.e., hypo-eutectic, eutectic , and hyper-eutectic. The effect of Si concentration on coating layer formation was studied by metallographic observation and EPMA analysis. Diffusion heat treatment of hot-dipped samples was also conducted and the change in the coating layer structure was examined. Metallographic examination showed that the adhered layers of samples hot-dipped in hypo-eutectic and eutectic Al-Si alloy baths are the same as the solidified structures of conventionally cast Al-Si Alloys. The $CrSi_2$-Al_X. phase was observed in the adhered coating layer of the sample hot-dipped in hyper-eutectic alloy. The amount of $CrAl_2$-Al_X increased with increasing bath temperature and immersion time. Fe-Al-Cr-Si alloy layers formed at the interface of the stainless steel and molten alloy, and grew to a maximum thickness of about 20 μm . The alloy layer growth rate and maximum thickness did not depend on Si concentration in the Al-Si alloy bath. (Japanese)

Galvanic Corrosion between Carbon Steel and Soldering Fluxes in a Concentrated LiBr Solution at High Temperatures

K. Mabuchi, T. Kikuchi, and H. Takahashi

J. Surf. Finishing Jpn., **49**, 875-880 (1998)

Galvanic corrosion between carbon steel and soldering fluxes was studied in a concentrated LiBr solution at 383 and 433 K, using extreme-value statistical analysis of pit depth in soldered parts, measurement of the amount of dissolved Fe^{2+} and dissolved flux components, and corrosion potential and galvanic current measurements. The soldering fluxes used were copper, copper alloys (Cu-Si-Mn, BAg-8, Ag30-Cu, 70/30-cupronickel), and nickel.

Nickel fluxes soldered with carbon steel caused considerable galvanic corrosion of carbon steel at 383 K, while carbon steel soldered with copper and copper alloy fluxes showed galvanic corrosion of the fluxes at 383 and 433 K. The galvanic corrosion rate of fluxes decreased in the order of copper > Cu-Si-Mn > Ag30-Cu > BAg-8 > 70/30-Cupronickel at 433 K, and Cu-Si-Mn > copper > Ag30-cu > BAg-8 > 70/30-cupronickel at 388 K. 70/30-cupronickel flux ws considered the most suitable soldering flux in a concentrated LiBr solution at high temperature. (Japanese)

High Temperature Oxidation of Refractory Metal Disilicides

K. Kurokawa

J. of High Temperature Soc., **24** (5), 161-166 (1998)

Some of silicides are receiving much attention as high-temperature structural materials having high oxidation resistance. In this review, high temperature oxidation behavior of refractory metal disilicides, notably molybdenum disilicide, was described. The topics are the effects of defects and H_2O vapor on accelerated oxidation of $MoSi_2$. (Japanese)

Accelerated Oxidation in $MoSi_2$
- Its Process and Influential Factors -

K. Kurokawa

Proc. of Resistance and Durability of Advanced materials
against High-Temperature Environment, JSCE, 1-9 (1998)

Although thermodynamical prediction shows that simultaneous oxidation of Mo and Si is not an intrinsic property of molybdenum disilicide ($MoSi_2$), it is well known that accelerated oxidation at low temeratures occurrs. The process and influential factors in the accelerated oxidation are described in this report. The simultaneous oxidation, namely accelerated oxidation, occurrs preferentially at defects such as pores and cracks and gradually spreads over the surface, resulting in pesting. In addition, H_2O vapor in air accelerates the occurrence of the simultaneous oxidation. As a result, the accelerated oxidation and pesting can be hindered by using fully dense $MoSi_2$. (Japanese)

Reformation of Anodic Oxide films on Aluminum after Destruction by pulsed Nd-YAG Laser Irradiation

M. Sakairi, Y. Ohira, and H. Takahashi

Proc. Intern. Symp. on Passivity and Its Breakdown, p. 643-653

Pulsed Nd-YAG laser was used to investigate the destruction and reformation of barrier type anodic oxide films on aluminum in a neutral borate solution and anodic polarization. Current transients after laser irradiation were measured by personal computer with A /D conversion system, to examine the effect of laser power, film formation potential, and applied potential on the oxide formation. By laser irradiation, the current increased instantaneously and then decreased exponentially with time, suggesting the inverse logarithmic growth rate law in the film formation after destruction by laser. The amount of charge obtained by integrating current transient curves between 0 and 600 ms linearly increased with increasing applied potential, and this suggested that the thickness of film formed at laser irradiated area is proportional to the applied potential. Current fluctuation was observed at the initial period of film formation for specimens covered with thick oxide films. The current fluctuation is discussed in terms of the specimen vibration due to the film destruction. (English)

Patterning of Aluminum Surface with Laser Irradiation and Nickel Electrodeposition. I. Removal of Anodic Oxide Films by Laser Irradiation

M. Sakairi, J. Wakabayashi, H. Takahashi, Y. Abe, and N. Katayama

J. Surf. Finishing Jpn., **49**, 1220-1226 (1998)

Fabrication of fine pattern on an aluminum surface with pulsed YAG laser irradiation and subsequent nickel plating has been reported in two consecutive papers. The first paper studies anodic oxide film removal from aluminum by laser irradiation.

Aluminum specimens covered with porous anodic oxide films were irradiated with one YAG laser pulse in air and in Ni^{2+} ion solutions to examine the effect of laser power, P, defocusing distance, Δx, and irradiation atmosphere on the size of film removed area.

Anodic oxide films were thoroughly removed by laser irradiation at $P > 2$ mW in both air and solution, when the specimen was placed near the focal plane of the laser beam. The size of film removed area increased with increasing P and showed a minimum on the focal plane ($\Delta x = 0$) , indicating 40 - 300 μm diameter, larger in solution than in air.

Oxide film removal by laser irradiation is discussed, focusing on laser ablation of the metal substrate. (Japanese)

Patterning of Aluminum Surface with Laser Irradiation and Nickel Electrodeposition. II. Local Nickel Deposition at Laser Irradiated Area and Patterning with Fine Ni-Lines.

M. Sakairi, J. Wakabayashi, H. Takahashi, Y. Abe, and N. Katayama

J. Surf. Finishing Jpn., **49**, 1227-1232 (1998)

Fabrication of fine pattern on an aluminum surface with pulsed YAG laser irradiation and subsequent nickel plating has been reported in two consecutive papers. The second paper studies nickel deposition on aluminum irradiated with a pulsed YAG laser, and pattern fabrication with nickel deposition.

Aluminum specimens covered with porous anodic oxide film were irradiated with a pulsed YAG laser in air and in Ni^{2+} ion solutions using a three dimensional stage controlled by computer, and then nickel was electrodeposited and studied potentiostatically as functions of cathode potential, E_c, Ni^{2+} ion concentration, C_{Ni}, and bath temperature, T.

Nickel was deposited only at the laser-irradiated area at potentials more negative than - 0.8 V (vs. sat.-AgCl/Ag), and deposition speeded up at higher C_{Ni} and T ,and more negative E_c. The current efficiency for nickel deposition was 95% between-1.10 and -1.40 V. During cathodic polarization, cathodic current, i_c, increased with time, t_c, to reach a steady value at $t_c < 1$ min for specimens laser-irradiated in the solution, whereas a longer period was needed to reach the steady value for the specimen irradiated in air. This suggests that thermal oxide films formed after anodic oxide film removal by laser irradiation in air inhibit nickel nuclei formation in the initial plating.

The Hokkaido University Symbol 7 mm in size was drawn on aluminum with nickel plating lines with different widths between 50 and 200 mm. (Japanese)

In-situ Joining of Nickel Monoaluminide to Iron by Reactive Sintering

Kiyotaka Matsuura, Kenichi Ohsasa, Noritoshi Sueoka and Masayuki Kudoh

ISIJ International, **35**, 310-315 (1998)

A cylindrical block of nickel monoaluminide. NiAl, is produced from a mixture of nickel and aluminum powders by sintering a powder compact under a pseudo-isostatic pressure, and is simultaneously joined to an iron block with the same shape. When the joining couple of the powder compact and the iron block is heated to approximately 900 K, a violent exothermic synthesis reaction, Ni +Al→NiAl, suddenly starts, and the temperature of the compact quickly rises owing to the heat of reaction and exceeds the melting point of NiAI, 1911 K. Because the molten NiAl wets the contacting surface of the iron block, an iron-rich NiAl-base alloy and an iron-base ternary solid solution are produced on each side of the joining interface. No cracks or cavities are formed in the NiAl even in the vicinity of the joining interface. Hardness continuously changes across the joining interface from approximately 330 in NiAl to approximately 55 in iron All of five specimens of a four-point bending test fractured in NiAl, the fracture surface being 1 to 2 mm away from the joining interface.

SHS of Intermetallics from Elemental Liquids and Simultaneous Joining to Structural Materials

Kiyotaka Matsuura, Kenichi Ohsasa, Tatsuya Ohmi, Hiroshi Jinmon
and Masayuki Kudoh

Proc., 1st Russian-Japanese Workshop on SHS, 14-17 (1998)

Molten aluminum and molten nickel have been stepwise cast onto a steel block. Molten nickel monoaluminide, NiAl, is synthesized by an exothermic reaction between the cast metals, and the NiAl is simultaneously joined to the steel, when it solidifies on the steel. Owing to the exothermic reaction, the temperature of the synthesized NiAl reaches approximately 2900 K which is approximately 1000 K higher than its melting point. A thin layer near the surface of the steel block melts, and iron dissolves in the molten NiAl, which yields an intermetallic compound of NiAl-Fe pseudo-binary system. Continuous concentration profiles of aluminum, nickel and iron appear across the joining interface between the intermetallic and the steel, which leads to a continuous micro-hardness profile across the interface. The joining strength was estimated to be higher than 220 MPa. The NiAl-base intermetallic was found to have an excellent resistance to wear, oxidation and corrosion.

Reactive Sintering of NiAl and Simultaneous Joining to Steel

Kiyotaka Matsuura, Kenichi Ohsasa, Noritoshi Sueoka, and Masayuki Kudoh

The Third Pacific Rim International Conference on Advanced Materials
and Processing, TMS, **2**, 2419-2424 (1998).

A block of nickel monoaluminide, NiAl, is produced from a mixture of nickel and aluminum powders by sintering a compact of the powder mixture under a pseudo-isostatic pressure, and it is simultaneously joined to a block of an ultra-low carbon steel. When the joining couple of the powder compact and the steel block is heated to approximately 900 K, an exothermic synthesis reaction, Ni+Al→NiAl, suddenly starts. The temperature of the compact quickly rises owing to the heat of reaction and exceeds the melting point of NiAl, 1911 K, while the temperature of the steel block rises to approximately 1300 K even in the center of the thickness of 15 mm. During the reaction period of 2 to 3 seconds, the molten NiAl wets the surface of the steel block and produce an iron-rich NiAl-base liquid alloy in the vicinity of the joining interface, while nickel and aluminum diffuse into the steel to produce a multi-component solid solution. The structure of NiAl consists of fine grains, particularly near the joining interface. No cracks or cavities are formed in the NiAl. Micro-hardness continuously changes across the joining interface from approximately 330 in the NiAl to approximately 55 in the steel. All of five specimens of a four-point bending test fractured in the NiAl, the fracture surface being 1 to 2 mm away from the joining interface.

Influence of the Al_2O_3 Sputtered Diffusion Barrier Film on $MoSi_2$/Nb Interface

S. Ohta, G. Ochiai, K. Kurokawa, H. Takahashi, and H. Kinoshita

Proc. of the 1998 Inter'l Sympo. on Adv. Energy Tech., 705-710 (1998)

Molybdenum disilicide ($MoSi_2$) is believed to be a promising intermetallic matrix for high-temperature applications. It offers oxidation resistance which is superior to most other intermetallics at elevated temperatures above 1273 K. $MoSi_2$ also retains high strength, stiffness and lower density in comparison with nickel-base superalloys. It is generally used to joint the various reinforcements based on refractory metals, for example Mo, Ta, or Nb, because obtaining the advantage of increasing toughness. The interface of $MoSi_2$/refractory metals joints produced by the plasma sintering method formed reaction products. Especially, on the $MoSi_2$/Nb, the reaction in the interface between $MoSi_2$ and Nb is severe as a result of Si diffusion into Nb. Therefore, Si concentration in MoSi decreases so that oxidation resistance reduces. One of solutions to retard it is to insert a diffusion barrier between $MoSi_2$ and Nb. However, the thickness of the diffusion barrier of about 10 micronmeter would affect mechanical properties. In this study, the diffusion barrier was produced by RF magnetron sputtering method, and the microstructural changes on processing $MoSi_2$/Nb joint was investigated by the transmission electron microscope (TEM). (English)

Interfacial Reaction Between Nb and $MoSi_2$ During Bonding Process

Kazuya KUROKAWA, Genzo OCHIAI, Hideaki TAKAHASHI
Heishichiro TAKAHASHI, and Shigemasa OHTA

Applied Plasma Science, **6**, 84-89 (1998)

To clarify the physico-chemical compatibility of Nb with $MoSi_2$, the bonding of $MoSi_2$ to Nb was performed by a spark plasma sintering method. The structures of the reaction layers formed in the interface during the process consisted of Nb /Nb_5Si_3/$(Mo,Nb)_5Si_3$/Mo_5Si_3/$MoSi_2$. The rate-dermining step in the growth of the reaction layer is thought to be Si-diffusion through the reaction layer. From these results, the reaction path and physico-chemical compatibility was discussed. (Japanese)

The Dependence of the Diffusion Coefficients of ^{3}H and Cs on Grain Size in Compacted Montmorillonite

Mamoru Nakajima, Tamotsu Kozaki, Hiroyasu Kato,
Seichi Sato and Hiroshi Ohashi

Scientific Basis for Nuclear Waste Management XXI, **506**, 947-948 (1998)

For performance assessment of bentonite buffer material in geological disposal of high-level radioactive waste, the particle size of bentonite and its effect on the diffusion behavior of radionuclides in compacted bentonite were studied. Bentonite samples with different particle sizes were prepared, and characterized by the BET and EGME methods for specific surface areas, by the laser diffraction/scattering particle size analysis for particle size distribution, and by SEM observations. Apparent and effective diffusion coefficients of tritiated water (HTO) and Cs^+ ions in compacted bentonite were also determined using bentonite samples with different particle sizes. With HTO, there were higher diffusion coefficients in fine-grained samples, but opposite particle size effects were observed with Cs^+ ions. These findings cannot be explained by the conventional pore water diffusion model, and suggest a different diffusion process for Cs^+ ions and also at higher dry density region. (English)

Self-diffusion of Sodium Ions in Compacted Sodium Montmorillonite

Tamotsu Kozaki, Atsushi Fujishima, Seichi Sato and Hiroshi Ohashi

Nuclear Technology, **121** (1), 63-69 (1998)

Diffusion of sodium ions through compacted sodium montmorillonite in a water-saturated state was studied to obtain fundamental information for performance assessments of geological disposal of high-level radioactive waste. Basal spacing obtained from XRD(X-ray diffraction) measurements indicated a decrease in the interlamellar spacing with increasing dry density of the montmorillonite; the three-water-layer hydrate was observed at low dry density ($\leq$ 1.3 Mg m^{-3}) and the two-water-layer hydrate was observed at high dry density ($\geq$ 1.6 Mg m^{-3}), whereas both were observed at dry densities between 1.4 and 1.5 Mg m^{-3}. Activation energies from 14.1 to 24.7 kJ mol^{-1} were obtained from the temperature dependence of the self-diffusion coefficients of sodium ions. Activation energies lower than that for the diffusion of sodium ions in free water were found for montmorillonite specimens with dry densities of $\leq$ 1.2 Mg m^{-3}, while higher activation energies were observed at dry densities $\geq$ 1.4 Mg m^{-3}. The pore water diffusion model, the general model used for migration of nuclides, is based on geometric parameters; however, findings cannot be explained by only the changes in the geometric parameters. Possible explanations for the dry density dependence of the activation energy are changes in the temperature dependence of the distribution coefficients of sodium ions on the montmorillonite, changes in the diffusion process with an increase in dry density, or both. (English)

Diffusion Mechanism of Cesium Ions in Compacted Montmorillonite

Tamotsu Kozaki, Hiroki Sato, Seichi Sato and Hiroshi Ohashi

Proceedings of the workshop on the "Microstructural modeling of natural and artificially prepared clay soils with special emphasis on the use of clays for waste isolation", Lund, Sweden, October 12-14, 1998, 214-220 (1998)

For the safety assessment of geological disposal of high-level radioactive waste, the diffusion behavior of Cs^+ ions in compacted Na- and Ca-montmorillonite mixtures was studied. The apparent diffusion coefficients of Cs^+ ions were determined as functions of the diffusion temperature and the ionic equivalent fraction of Ca^{2+} ions. The apparent diffusion coefficients were almost constant at higher temperatures, 323 and 313 K, while they decreased with increasing ionic equivalent fraction at lower temperatures, 298 and 288 K. The activation energies for diffusion of Cs^+ ions were also determined from the temperature dependence of the apparent diffusion coefficients at each ionic equivalent fraction. The activation energy increased from 34 kJ mol^{-1} to 38 kJ mol^{-1} as the ionic equivalent fraction increased from zero to 0.75, after which it increased steeply and reached 49 kJ mol^{-1} at the ionic equivalent fractions of 0.94 and 1.0. The pore water or surface diffusion models cannot explain these findings. Interlayer diffusion is suggested as the most probable explanation for the diffusion of Cs^+ ions. (English)

Activation Energy for Diffusion of Chloride Ions in Compacted Sodium Montmorillonite

Tamotsu Kozaki, Nobuhiko Saito, Atsushi Fujishima, Seichi Sato
and Hiroshi Ohashi

Journal of contaminant hydrology, **35**, 67-75 (1998)

Diffusion of chloride ions in compacted montmorillonite was studied for a performance assessment as buffer material in geological disposal of high-level radioactive waste. The apparent diffusion coefficients were from 6.8×10^{-12} to 2.2×10^{-10} $m^2\ s^{-1}$ for sodium montmorillonite at dry densities from 1.0 to 1.8 Mg m^{-3} at diffusion temperatures from 278 to 323 K. The activation energy increased from 14 kJ mol^{-1} (lower than that in free water, 17.4 kJ mol^{-1}) to 25 kJ mol^{-1} (higher than that in free water), as the dry density increased from 1.0 to 1.8 Mg m^{-3}. These facts can be attributed to changes in the predominant diffusion process as dry density increases. Conventional diffusion models, such as the pore water diffusion model cannot explain the dry density dependence of the activation energy. (English)

Effect of pH on Stability Constants of Sr(II)-Humate Complexes

Mohammad Samadfam, Takashi Jintoku, Seichi Sato and Hiroshi Ohashi

J. Nucl. Sci. Technol., **35**, 579-583 (1998)

The apparent stability constant, β, for the complexation of Sr(II) with humic acid(HA) was determined by a dialysis method in the pH range from 4 to 10 at ionic strength of 0.1 mol/dm^3($NaClO_4$) at 298 K under N_2 atmosphere. It was found that logβ increased with pH from 2.5 at pH 4.0 to 4.1 at pH 10.0. The logβ tended to level off at higher pHs, indicating that saturation was being reached. Further, the apparent ligand to metal ratio was found to be 1.15 ± 0.10. Dissociation of carboxylic and phenolic groups of HA with pH is probably the main factor that gives rise to the changes in stability constants. (English)

Effects of Humic Acid on the Sorption of Eu(III) onto Kaolinite

Mohammad Samadfam, Seichi Sato and Hiroshi Ohashi

Radiochim. Acta, **82**, 361-365 (1998)

Sorption coefficients of Eu (III) on kaolinite were measured at pH from 3.5 to 8.5 and humic acid (HA) concentration of 0 to 20 ppm at ionic strength of 0.1($NaClO_4$). The Eu (III)-humate stability constants were also measured at the same ionic strength at pH from 3.3 to 5.5. In the absence of HA, the sorption coefficients of Eu (III) ions increased with pH over the whole pH range. By introducing HA, the sorption coefficients were enhanced at pH up to around 6, above which there was a considerable decrease in the coefficients. Sorption of HA-bound Eu (III) onto kaolinite results in higher sorption coefficients at low pH, while sorption of the HA-bound Eu (III) at higher pH decreases. The effects of Humic acid were interpreted by a model based on the stability constant of Eu (III)-humate complexes, fractional sorption of HA on kaolinite, and sorption coefficient of Eu (III) on kaolinite in the absence of HA. The model was found to be in fairly good agreement with the experimental data. (English)

Thermal Expansion and Thermal Conductivity of Cesium Uranates

Masahide Takano, Kazuo Minato, Kousaku Fukuda, Seichi Sato, Hiroshi Ohashi

J. Nucl. Sci. Technol., **35**, 485-493 (1998)

Two kinds of cesium uranates, which are often predicted by thermochemical calculations to be formed in irradiated oxide fuels with high oxygen potentials, were prepared from U_3O_8 and Cs_2CO_3 to determine the thermal expansions and the thermal conductivities. The lattice parameters of tetragonal Cs_2UO_4 and monoclinic $Cs_2U_2O_7$ were measured by the high-temperature X-ray diffraction method as a function of temperature. The linear thermal expansions of Cs_2UO_4 and $Cs_2U_2O_7$ obtained from the temperature dependence of the lattice parameters were 1.2% and 1.1% from room temperature to 973 and 1073 K, respectively. The thermal diffusivities of Cs_2UO_4 and $Cs_2U_2O_7$ were measured on the disk-shaped samples by the laser flash method as a function of temperature. The thermal conductivities were evaluated from the measured thermal diffusivities and the bulk densities, and the specific heat capacity available in the literature. The thermal conductivity of Cs_2UO_4 corrected for 100% TD was 1.2 W/m · K at 980 K and that of $Cs_2U_2O_7$ was 0.94 W/m · K at 1093 K, which are about 30 % and 27 % of that of UO_2, respectively.

Thermal Expansion and Thermal Conductivity of Cs_2CrO_4

Masahide Takano, Kazuo Minato, Kousaku Fukuda, Seichi Sato, Hiroshi Ohashi

J. Alloys Comp., **278**, 277-282 (1998)

The temperature dependence of the lattice parameters of Cs_2CrO_4 was measured by the high-temperature X-ray diffraction method from 293-873 K. The linear thermal expansion of Cs_2CrO_4 obtained from the temperature dependence of the lattice parameters was 2.34% at 873 K, which was about four times that of UO_2 and more than twice that of stainless steel (SUS 316). The thermal diffusivity of Cs_2CrO_4 was measured by the laser flash method from 296-1040 K. The thermal conductivity of Cs_2CrO_4 was evaluated from the measured thermal diffusivity and bulk density, and the specific heat capacity from the literature. The thermal conductivity of Cs_2CrO_4 corrected for 100%TD remained almost constant up to 500 K, increased with temperature above 500 K, and it was 0.40 W $m^{-1}K^{-1}$ at 800K, which was less than 10 and 12 % of those of UO_2 and $U_{0.8}Pu_{0.2}O_{1.98}$, respectively. (English)

Abstracts of Publications

Confirmation of the Changes of Isotopic Distribution for the Elements on Palladium Cathode after Strong Electrolysis in D_2O Solution

Tadahiko Mizuno, Tadayoshi Ohmori and Michio Enyo,

Int. J. Society of Materials Engineering for Resources, **6** (1), 45-59 (1998)

Many elements on Pd electrode were confirmed by several analytic methods; reaction products with the mass number up to 208 are deposited on palladium cathodes, which were subjected to electrolysis in a heavy water solution at high pressure, temperature, and current density for prolonged time. These masses were composed of many elements ranged from hydrogen to lead. Extraordinary observations were the changes of their isotopic distributions in the produced elements; these were radically different from the natural ones. For example, natural chromium is 4.3% Cr-50, 84% Cr-52, 9.5% Cr-53 and 2.4% Cr-54. But the Chromium found on the Pd surface was 14% Cr-50, 51% Cr-52, 2.4% Cr-53 and 11% Cr-54. Natural Isotopic distribution varies by less than 0.003% for Cr. Essentially the same phenomenon was confirmed eight times with high reproducibility at high cathodic current density, above 0.2A/cm^2. All the possibilities of contamination had been carefully eliminated by several pretreatments for the sample and electrolysis system. It means that a nuclear reaction had taken place during the electrochemical treatment. It is indicating the role of new interactions discovers in the framework of a generalization of the usual quantum mechanics. Evidently such new interactions, due to the mutual overlap of wavepackets, should explain the new phenomenologies that are experimentally observed in this study. (English)

Nuclear Transmutation Reaction Occurring during the Light Water Electrolysis on Pd Electrode

Tadayoshi Ohmori, Tadahiko Mizuno, Kazuya Kurokawa and Michio Enyo

Int. J. Society of Materials Engineering for Resources, **6** (1), 35-44 (1998)

Certain amounts of unexpected elements, Hg. Au, Fe, Cu, Zn, and K with the different isotopic contents evidently different from their natural isotopic abundance were found to be produced on/in Pd electrode by the light water electrolysis. The amounts of Fe and Cu reached several atomic percent in the vicinity of the electrode surface. These elements were distribution of Au was completely overlapping with that of Pd partially deposited on the scraped edge of the Pd electrode. (English)

Detection of Radiation Emission, Heat Generation and Elements from a Pt Electrode Induced by Electrolytic Discharge in Alkaline Solutions

Tadahiko Mizuno, Tadayoshi Ohmori, Tadashi Akimoto and Yoshiaki Aoki

Proceedings of the Intersociety energy conversion engineering conference,
August 2-6,1998, Colorado springs, Colorado, USA, I-1868

Radiation emission. heat generation and detection of elements were confirmed during electrolytic discharge at high voltage in a light and heavy water solution containing an alkaline ion from the platinum electrode. We employed simple temperature measurement techniques, the He-3 neutron detector and a NE-213 scintillator to measure the emission and energy distribution, energy dispersive x-ray analysis (EDX) and secondary ion mass spectroscopic measurement (SIMS) for the elements isotopic distributions. We counted up to several million-radiation emissions per second by the counter. High heat output of the order of several hundred watts was observed from input power of tens of watts. The detected counts by the He-3 detector increased with discharge time after an induction period, and showed radical fluctuations. The counting rate were decreased 1/10 by cadmium shield, meanwhile the Copper and iron shield showed no count changes. The rate of emission increased with the input volt. Moreover, the rate was increased with the concentration of the ions and their mass number. Their rate was ten times higher in heavy water than light water solution. The emission rate corresponded linearly with the input current, except at the low input coulomb range due to induction time. From this linear relation, it was observed that the typical dependence of the count/current during 1 hour was 10^6 /s/A/cm^2 for a platinum electrode in 0.5 molar potassium carbonate of heavy water solution. We analyzed the Pt electrode surface after discharge by EDX, EPMA and SIMS measurements. Many elements were found: Ca, Cr, Fe, Ti, Cu, Zn and Pd. Most of these were not found in significant quantities as impurities in the solution or cell materials, especially not Zn or Pd. Notably, Zn and Pd, both of which were absent in the original solution, were found to have isotope ratios radically different from their natural abundance. This was particularly noticeable in the case of Pd. The isotope shifts mainly occurred at the electrode surface within 1 micrometer. We can conclude that a nuclear reaction would be induced by the electric discharge on the metal surface in the solution. The reaction probably took place in the thin layer between the electrolyte and electrode. (English)

Transmutation in A Gold-Light Water Electrolysis System

Tadayoshi Ohmori, Tadahiko Mizuno, Yoshinobu Nodasaka and Michio Enyo

Fusion Technology, **33**, 367-382 (1998)

Mercury, krypton, nickel, and iron with anomalous isotopic compositions were found to be produced on or in gold electrons during light water electrolysis. In addition, silicon and magnesium with anomalous isotopic compositions were also detected in the precipitates separated from the gold electrode electrolyzed at extremely high current densities. After the electrolysis, the surface of the electrode exhibited an extraordinary structure, i.e., a number of microcrater like volcanoes were developed. The structure of the outside wall of the craters was very much like that of the precipitates, and hexagonal crystallite layers in the inside wall of the craters suggested a partial recrystallization of the electrode material due to some intense heat evolution. The craters developed along the rim of the microcracks, and scraped edges of the electrode. These results suggest that some nuclear transmutation reactions occur during the electrolysis to produce these effects. (English)

Probability of Neutron and Heat Emission from Pt Electrode Induced by Discharge in the Alkaline Solution

Tadahiko Mizuno, Tadayoshi Ohmori and Tadashi Akimoto

Proceedings of The seventh international conference on cold fusion,
April 19-24,1998, Vancouver, Canada, Organized by Fred Jaeger 247-252 (1998)

Probability of the production of neutrons was discussed during electrolytic discharge at high voltage in a light and heavy water solution containing an alkaline ion. We employed a He-3 neutron detector and a NE-213 scintillator to measure neutron emission and energy distribution. We counted up to several million neutrons per second. High heat output of the order of several hundred watts was observed from input power of tens of watts. The neutron counts detected by the He-3 detector increased with discharge time after an induction period, and showed radical fluctuations. Absorption of neutrons by cadmium showed them to be thermal. Copper and iron showed no count changes. The rate of neutron emission increased with the input volt. Moreover, the rate was increased with the concentration of the ions and their mass number. Their rate was ten times higher in heavy water than light water solution. The neutron emission rate corresponded linearly with the input current, except at the low input coulomb range due to induction time. From this linear relation, it was observed that the typical dependence of neutron emission /current during 1 hour was 1000000 /s/A/cm^2 for a platinum electrode in 0.5 molar potassium carbonate of heavy water solution. We can conclude that a nuclear reaction would be induced by the electric discharge on the metal surface in the solution. The reaction probably took place in the thin layer between the electrolyte and electrode. (English)

Detection of Radiation Emission, Heat Generation and Elements from a Pt Electrode Induced by Electrolytic Discharge in Alkaline Solution

Tadahiko Mizuno, Tadayoshi Ohmori and Tadashi Akimoto

Proceedings of The seventh international conference on cold fusion,
April 19-24,1998, Vancouver, Canada, Organized by Fred Jaeger 253-258, (1998)

Production of neutrons was confirmed during electrolytic discharge at high voltage in a light and heavy water solution containing an alkaline ion. We employed a He-3 neutron detector and a NE-213 scintillator to measure neutron emission and energy distribution. We counted up to several million neutrons per second. High heat output of the order of several hundred watts was observed from input power of tens of watts. The neutron counts detected by the He-3 detector increased with discharge time after an induction period, and showed radical fluctuations. Absorption of neutrons by cadmium showed them to be thermal. Copper and iron showed no count changes. The rate of neutron emission increased with the input volt. Moreover, the rate was increased with the concentration of the ions and their mass number. Their rate was ten times higher in heavy water than light water solution. The neutron emission rate corresponded linearly with the input current, except at the low input coulomb range due to induction time. From this linear relation, it was observed that the typical dependence of neutron emission/current during 1 hour was 1000000 /s/A/cm^2 for a platinum electrode in 0.5 molar potassium carbonate of heavy water solution. We conclude that a nuclear reaction was induced by the electric discharge on the metal surface in the solution. The reaction probably took place in the thin layer between the electrolyte and electrode. (English)

Strong Excess Energy Evolution, New Element Production and Electromagnetic Wave and/or Neutron Emission in the Light Water Electrolysis with a Tungsten Cathode

Tadayoshi Ohmori and Tadahiko Mizuno

Proceedings of The seventh international conference on cold fusion,
April 19-24,1998, Vancouver, Canada, Organized by Fred Jaeger 279-284, (1998)

Strong heat evolution enough to incandesce the electrode was observed by applying a high electric power. The excess energy amounts to 183 W, which is 2.6 times the input power. At the same time strong electromagnetic wave and/or neutron emission reaching 60000 counts/s by a neutron counter was observed. During the electrolysis considerable amounts of new elements, i.e. Pb, Fe, Ni, Cr and C were produced. The distributions of Fe, Cr and C on/in the electrode was overlapped. The isotopic distribution of Pb deviated greatly from the natural isotopic abundance. These results show that the nuclear transmutation reaction took place on/in the tungsten electrode during the electrolysis. (English)

A kinetic Model of the Dissolution of Magnetite (Fe_3O_4) in EDTA Solutions

- Estimation of the Dissolving EDTA Species -

H. Tamura, S.Takasaki, and R. Furuichi

Bunseki Kagaku (J. Jpn. Soc. for Anal. Chem.), **47** (7), 397-403 (1998)

Magnetite, an iron oxide present under reducing conditions, is a component of soils, iron ores, corrosion scales on iron and steels, and others. For a wet analysis of magnetite in samples, magnetite is preliminarily dissolved; the precision and accuracy of the final analytical results are greatly influenced by the dissolution process. A dissolution model would be useful in the design of dissolution processes and control of the optimum dissolution conditions for particular analytical purposes. Here, modeling was made for the kinetics of the dissolution of magnetite in EDTA (H_4Y) solutions by assuming the following successive reactions: 1) chelation of the Fe ion sites on Fe_3O_4 with $H_nY^{(4-n)-}$, and the transfer of Fe chelates to the solution; 2) the reaction of the oxide ion sites left behind on Fe_3O_4 with protons, and the transfer of the formed water to the solution. The derived rate equation reproduced the time-course of the dissolved Fe concentration and the Fe concentration peaks at pH 2.3. For five EDTA species with different proton numbers (n=0~4), the resulting model parameters (rate constants) were examined in the pH range 1.5 ~ 3.3. From the pH dependence of the model parameters, H_2Y^{2-} was estimated to be the most likely dissolving EDTA species in solution. (Japanese)

Surface Acid-Base and Charge Characetristics of Metal Oxide Particles and Affinities of Ions for Oxides

H. Tamura

Resources Processing, **45** (4), 276-281 (1998)

Metal oxide particles in aqueous solutions have electric charges due to the (de)protonation of acid-base surface hydroxyl groups formed by dissociative chemisorption of water molecules. The charges adsorb anions and cations from the solution to maintain electric neutrality, resulting in ion exchange. The amount of surface charge was measured as a function of pH by titration, and the ion-exchange reactions accompanying the charge formation were modeled by using the Frumkin isotherm, which assumes suppression of the reaction due to lateral interactions between the interphase species. From the model parameters, it was found that the intensity of cation exchange (deprotonation) increases in the order: $Al_2O_3 < Fe_3O_4 < TiO_2 < MnO_2$, and the intensity of anion exchange (protonation) decreases in the same order. The electronegativity of the lattice metal ions of these oxides was estimated and found to increase in the order above. It is suggested that, with electronegativity of the lattice metal ions, the electron density and hence the acid-base nature of hydroxyl sites changes. Also, the adsorption affinity of alkali metal ions was evaluated and it is suggested that these ions are adsorbed in the hydrated form. (Japanese)

Polyfunctionality of Carboxyl Sites on IRC-50, an MR-type Ion Exchange Resin, Evaluated by Modeling with the Frumkin Isotherm

H. Tamura, M. Kudo, and R. Furuichi

Reactive and Functional Polymers, **38**, 177-181 (1998)

For efficient and adequate recovery or removal of ions by ion exchange, it is important to know the properties of ion-exchange resins quantitatively. The exchange properties of Amberlite IRC-50, a macroreticular type weak acid cation-exchange resin, were measured by titration. The properties were modeled by considering ion-exchange sites with different reactivities (polyfunctionality) and suppression of ion exchange with the progress of the reaction due to repulsive lateral interactions between adsorbed ions. It was found that there are two types of sites with similar ion-exchange intensities but different lateral interactions. The different properties of ion-exchange sites were ascribed to the micro- and macropore environments of the resin. Further, the adsorption affinity of alkali metal ions for the two types of sites was discussed in terms of the hydrated ion sizes and the complex formation with carboxyl group sites. (English)

Growth Rate Constant and Chemical Diffusivity in Silicides MO_5Si_3 and Ta_5Si_3

Francis Christian, Hideaki Sohma, Toshiaki Tanaka, Hiroyuki Tanaka,
Kenichi Ohsasa and Toshio Narita

Mater. Trans. JIM, **39**, 286-291 (1998)

The growth kinetics and chemical diffusion coefficients in intermetallic silicides M_5Si_3 (M = Mo and Ta) were investigated at temperatures between 1273 and 1673 K in a vacuum capsule using Mo/$MoSi_2$ and Ta/$TaSi_2$ couples, where both disilicides were coated on Mo and Ta substrate by a CVD method. It was found that both the M_5Si_3 layers grew parabolically. Concentration profiles of Si, Mo and Ta were measured across cross-sectioned samples using an electron-probe microanalysis and chemical diffusion coefficients were obtained using Wagner's equation on multi-layer diffusion systems. Both the parabolic rate constant and chemical diffusion coefficient in the Mo_5Si_3 phase were approximately one order of magnitude larger than those of the Ta_5Si_3 phase. Activation energy for the parabolic rate constant was close to that of the chemical diffusion coefficient for each diffusion couple, showing 297 and 271 kJ/mol for the Mo_5Si_3 and Ta_5Si_3 phases, respectively. Microstructural observations indicated that Kirkendall voids formed within the Mo_5Si_3 layer close to the $MoSi_2$ phase, whereas there is little formation of voids in the Ta_5Si_3 layer.

Siliconizing of Molybdenum Metal in Indium-Silicon Melts

Francis Christiant and Toshio Narita

Mater. Trans. JIM, **39**, 658-662 (1998)

Siliconizing of Mo to form a silicide layer was investigated in the In-Si melt alloy with a two phase mixture of a solid Si and an In-Si melt at temperatures between 1273 and 1473 K for up to 90 ks in a vacuum ampoule. The $MoSi_2$ layer was grown in thick because an activity of silicon in the melt alloy is close to unity, accompanied by a formation of a thin Mo_5Si_3 layer between the $MoSi_2$ layer and Mo substrate. These two layers grew in accordance with a parabolic rate raw. Chemical diffusion coefficients in both the $MoSi_2$ and Mo_5Si_3 layers were obtained using Wagner analysis for the diffusion couple of a $Mo/Mo_5Si_3/MoSi_2/Si$ (in the melt). Activation energies for the growth rate constants are 157 kJ /mol for the $MoSi_2$ and 350 kJ /mol for the Mo_5Si_3, respectively, and they are the same as those for chemical diffusion coefficients due to the fact that terminal compositions of 37.5 and 39.1 at%Si for both sides of the Mo_5Si_3 layers are almost independent of temperature. Composition of 39.1 at%Si was coincided with the measured one for the two $MoSi^{2+}$ Mo_5Si_3 phase alloy, which was smaller than 40 at%Si cited in the phase diagram. Duplex layer structure and its growth kinetics in the present In-Si melt method were consistent with those obtained in the CVD method.

Coating Layer Modification in Zn-Al Hot-Dipped Steel Bolts

Junichi Tanaka, Mitsugu Sakaguchi and Toshio Narita

The Journal of the Surface Finishing Society of Japan, **49**, 1105 - 1110 (1998)

Modification of steel bolt coating layers was studied using two step Hot-Dipping. The sample was at first dipped into primary Zn melt , and successively into secondary Zn-7mass %Al melt . To clean the steel surface , and prevent it from oxidation , two fluxes , aqueous solution and molten salt , were used before the first dip. The formation and morphology of the coating layer were studied using SEM and EPMA . When the aqueous solution flux was used , an alloy layer consists of a palisade δ_1 phase and granular (δ_1 +η) phases , and an ξ phase was formed on the steel surface after the dipping into primary Zn melt. In the sample pretreated with molten salt flux ,δ_1 phase grew thickly from the steel surface , and ξ phase grew successively , and minimal (δ_1 +η) phases were observed. The alloy layer thickness formed after dipping into secondary melt was controlled by the morphology of the alloy layer formed at the first dipping , i.e., if the alloy layer includes η phase , Fe_4Al_{13}-Zn_X phase , formed by the reaction with Zn-Al melt , is dispersed , resulting in spalling and dislodgment of the alloy layer during centrifugation. When the molten salt flux was used , uniform coating layer thickness more than 50 µm was obtained in two step Hot-Dipping. (Japanese)

Effect of Water Immersion and Surface Treatment on Esthetic Orthodontic Wires

Kazunori Nagayama, Fumio Watari, Toru Imai, Shuichi Yamagata
and Masahiro Kobayashi

Hokkaido J. Dent. Sci., **19** (2), 197-214 (1998)

For the development of an esthetic transparent orthodontic wire with fiber reinforced plastic structure (FRP wire) it was the most important theme to investigate the behavior in oral environment and give the sufficient durability for clinical application. After FRP wire was immersed in water at 37°C up to 30 days, 3 point bending test was done with the deflection 2 mm in the gauge length 14mm to evaluate the change in the mechanical properties through water immersion. The deactivating load and elastic recovery in hysterisis loop were decreased to a large extent after water immersion. The debonding of glass fiber / matrix interface and the fracture of glass fibers were observed by scanning electron microscopy, which was attributed to the phenomenon due to water absorption. To prevent this phenomenon the various coating was done after FRP wire was treated with the surface agent suitable to each coating material. Silicone rubber and polytetrafluoroethylene had not sufficient effects in water proof. Bis-GMA coated wire showed a good elastic recovery after immersion. The coating was done by either rolling, dipping or their mixed (R&D) methods. The lifting speed was changed from 1 to 6 cm/min. in dipping. The rolling and dipping methods, which produced the average film thickness 52 μm and 77 μm, respectively, did not show the sufficient effects of coating. The best result was obtained in R&D method with 1cm/min in dipping speed and the coating film thickness 117μm. The results of 100°C water immersion were qualitatively similar to those of 37°C, and the durability of the coating film could be evaluated in the short term. In the 37°C water immersion test, the non-coated FRP wire showed that the ratio of the deactivating to activating loads (deload/load ratio:D/L) at 1 mm in deflection dropped to about 20% after 10day immersion, while the FRP wire coated with Bis-GMA by the best method, that is, R&D method in dipping speed 1cm/min., showed the sufficient retention of flexural load (D/L 60～80%) and good elastic recovery even after 30 days. These results suggest that it is be possible to make lower the influence of water immersion upon the FRP wire and apply for clinics with the further improvement of coating treatments.

Imaging of Gradient Structure of Titanium/Apatite Functionally Graded Dental Implant

Fumio Watari, Atsuro Yokoyama, Fuminori Saso, Motohiro Uo,
Hironobu Matsuno and Takao Kawasaki

J. Japan. Inst. Metals, **62** (11), 1095-1101 (1998)

Various imaging methods were applied to observe and evaluate the functionally graded structure of dental implant and tissue reaction around the implant inserted in an animal experiment. To optimize the mechanical properties and biocompatibility the dental implant with the graded structure that increases the content of hydroxyapatite(HAP) in the longitudinal direction, from pure titanium(Ti) at one end up to 20% or 100%HAP at the other end, was fabricated through the process of powder metallurgy. After the external appearance was observed either with the naked eye or by optical microscopy, X-ray tranmission image was taken. The cross-section was then investigated by the secondary electron image and the compositional image using reflection electrons in a scanning electron microscope, line analysis and elemental mapping in EPMA(electron probe microanalysis) and the features of these methods were compared. All the methods for the optical images based on the reflection and scattering of light due to surface morphology, the X-ray transmission and reflection electron images based on the atomic number dependence , line analysis and mapping based on the characteristic X-ray emission confirmed the gradient structure. For the observation of the new bone formation around the implant which was inserted in the femora of rats, the compositional image by reflection electrons and EPMA elemental mapping were applied. These imaging methods whose contrast is based on the electronic structure of the specimens have the features that specimen preparation is simple without ultra thin sectioning and staining, and the recognition and evaluation of new bone area is easy. It would be more effective to use together with the conventional method to observe histologically the stained thin specimen by optical microscopy.

Mechanical Properties and Estheticity of FRP Orthodontic Wire Fabricated by Hot Drawing

Toru Imai, Fumio Watari, Shuichi Yamagata, Masahiro Kobayashi,
Kazunori Nagayama and Shinji Nakamura

Biomaterials, **19** (23), 2195-2200 (1998)

The FRP wires of the diameter 0.5mm with the multiple fiber structure were fabricated by drawing of fiber-polymer complex at 250°C for an esthetic, transparent orthodontic wire. Biocompatible $CaO-P_2O_5-SiO_2-Al_2O_3$(CPSA) glass fibers of 8-20 μm in diameter were oriented unidimensionally to the longitudinal direction in PMMA matrix. The mechanical properties were investigated by 3 point flexural test. FRP wire showed the sufficient strength and a very good elastic recovery after deformation. Young's modulus and the flexural load at deflection 1mm were nearly independent of fiber diameter and linearly increased with the fiber fraction. The dependence on fiber fraction obeys very well the rule of mixture. This FRP wire could 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. The estheticity in external appearance was excellent. Thus the new FRP wire can satisfy both mechanical properties necessary for an orthodontic wire and enough estheticity, which was not possible for the conventional metal wire.

Properties and Cytotoxicity of Water Soluble Na_2O-CaO-P_2O_5 glasses

Motohiro Uo, Morimichi Mizuno, Yoshinori Kuboki, Akio Makishima
and Fumio Watari

Biomaterials, **19**, 2277-2284 (1998)

Various compositions of Na_2O-CaO-P_2O_5 glasses are prepared to estimate glass formation, dissolution properties and cytotoxicity. In the wide composition range of 40mol% of P_2O_5 or more, clear glass samples were obtained. The estimated glass forming region was consistent with other ternary phosphate glass systems. The glass transition temperatures and crystallization temperatures decreased with increasing P_2O_5 content and increased with CaO content. Dissolution properties in distilled water and simulated body fluid (SBF) were measured. In distilled water, CaO free glasses showed extremely fast dissolution. The dissolution rate decreased with increasing CaO content and decreasing P_2O_5 content. This composition effect results from cross-link formation between the non-bridging oxygens of two different chains by Ca^{2+} ions which improves the phosphate network strength. In SBF, the dissolution rate followed a similar trend, but glass dissolution was suppressed. This suppression occurred due to the existence of soluble species of glass such as Na^+, Ca^{2+} and HPO_4^{2-}. The cytotoxicity decreased with increasing CaO content and with decreasing $PO_{2.5}$ content. This was the result of a change in pH and ion concentration in the medium.

The Effect of Rare-earth Oxides on the Crystallization of $CaO-Al_2O_3-SiO_2$ Glasses.

Motohiro Uo, Hiromitsu Seto, Kazuki Morita, Hiroyuki Inoue and Akio Makishima

Journal of Materials Science, **33**, 749-754 (1998)

$CaO-Al_2O_3-SiO_2-La_2O_3-Nd_2O_3$ glass was prepared and their physical properties, such as density, glass transition temperature and crystallization temperature were measured. The heat treatment of these glasses precipitated $Ca_2La_8(SiO_4)_6O_2$ oxyapatite (CLS) crystal for $20CaO-10Al_2O_3-60SiO_2-10La_2O_3$ (mol%) glass and $Ca_2Nd_8(SiO_4)_6O_2$ oxyapatite (CNS) crystal was precipitated with Nd_2O_3 substitution. Crystallization of these glasses was observed at the surface and internally within the samples. The spherical and stick like crystals were observed throughout the bulk of the glasses and the surface crystal layer of oxyapatite crystals were strongly oriented along the c-axis.

The apparent activation energies of crystal growth were estimated as 360kJ/mol.

The Fabrication and Properties of Aesthetic FRP Wires for Use in Orthodontics

Fumio Watari, Shuichi Yamagata, Toru Imai, Masahiro Kobayashi
and Shinji Nakamura

Journal of Materials Science, **33**, 5661-5664 (1998)

Transparent or translucent fibre-reinforced polymeric wires have been produced in an attempt at reproducing the mechanical properties of the metallic wires in current use in orthodontics. Two methods were employed-mould polymerisation or hot-drawing. Both methods produced wires 0.5 mm in diameter. Two polymers were investigated-poly(methyl methacrylate) and epoxy resin, and these were filled with either long, silane-coated alumina fibres or fibres made from CPSA glass. Whilst mould-polymerised wires showed a linear increase in Young's modulus with fibre content, they did not obey the rule of mixtures. However, the hot-drawn wires did, and they also demonstrated the rigidity, strength and good elastic recovery needed for use in orthodontics.