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Current topics on research are in the following:

(1) Electrochemical cycle system for recovery of aluminum from scrap aluminum.

An Al-Cl_2 chemical cell, one component step of the electrochemical cycle system, has been investigated focusing the development of an effective three-phase reaction zone. In order to enlarge the area of the reaction zones and elevate the concentration of chlorine gas in them, a stacked disk electrode rotating around an axis a little inclined to the horizontal was developed and the performance under different rotation speeds was studied in chloride melts containing $AlCl_3$ at about 750℃.

The other component steps of the system are also under investigation.

(2) Electrorefining of Al from scrap aluminum in a bipolar electrode system.

For electrorefining of Al from scrap aluminum by using a bipolar electrode system, an available molten salt predominantly composed of chloride was developed. The effect of co-existing metals in anode alloys, Cu, Fe, Mg and Si, was investigated together with the polarization characteristics of both electrodes, Al-Cu alloy anodes and a graphite cathode.

(3) Recovery of Al from Al-casting dross.

To recover Al from dross which is produced from Al casting industries, the components of the dross and their solubility in molten salts mainly composed of chlorides are under investigation.

(4) Corrosion test of steel and iron covered with an electrodeposited Al.

To measure oxygen reduction current on corroding surfaces, a flow cell in which it was possible to change flow passes of electrolyte through the test chamber was developed, and the attempt to determine the oxygen reduction current on corroding steel and iron covered with Al is being carried out.

(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 the eutectic composition of binary tin alloys, Sn-Zn, Sn-Bi and Sn-Ag, in a dilute sulfuric acid are in progress. The quantities of components of the alloys dissolved in the solution are being determined, and the corrosion resistance is being evaluated compared with the results from Sn-Pb alloy.

(6) 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.

An *in situ* technique composed of combined IR-RAS and QCM has been developed. By using this technique, the thickness of sulfite and water layers on copper specimens was determined. The band shifts in the IR-RAS spectra from that of the transmission spectra of several corrosion products were theoretically calculated.

(7) Copper corrosion and its prevention

The inhibition performance of newly-developed benzotriazole derivatives was evaluated for copper and copper alloys by immersion tests, electrochemical polarization as well as electrochemical impedance techniques and SERS technique.The localized "Ant's Nest"corrosion in copper tubes for heat-transfer units was studied in a simulated atmosphere in the presence of volatile organic substances, such as aldehydes, alcoholes and ketones.

(8) Protection of rebar in concrete

Corrosion protection of rebar in reinforced concrete structures has been studied by making use of waste galvanized steel fibers.

Other activities:

Professor S. Duan, Department of Physical Chemistry, USTB, visited this laboratory on July 30.

Prof. T. Ishikawa and Dr. M. Ueda attended the 5th Internatinal Symposium on Molten Salt Chemistry and Technology which was held in Dresden, Germany, in August and presented a paper entitled "Electrorefining of Aluminum Containing Fe-, Mg- and Si-Components" . Afterward they participated the 1997 Joint International Meeting- the 192nd Meeting of the Electrochemical Society and the 48th Annual Meeting of International Society of Electrochemistry-, Paris, France, and Assoc. Prof. T. Sasaki and Mr. Itoh joined to them. They presented two papers entitled *In situ* IR-RAS investigation of water in the layer formed on copper in a corrosive gas environment and Water layer on gold as investigated by *in situ* simultaneous measurement with IR-RAS and QCM. Dr.T.Notoya was invited as a keynote speaker to "Corrosion & Prevention 97"conference, November 9-12th,in Brisbane, Australia, by Australasian Corrosion Association.

Presentations

Reduction of Oxidant on a Passive Film on 430 Stainless Steel; H. Nakagawa, T. Sasaki and T. Ishikawa: The Joint Meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn, Surf. Finish. Soc. Jpn, and Jpn. Soc. Corros. Eng. Sapporo, Jan., 1997.

IR-RAS Spectra of a Thin film on Metals; J. Itoh, T. Sasaki and T. Ishikawa: ibid.

Performance of an Al-Cl_2 Chemical Cell -A Chlorine Electrode Rotating around a inclined Axis-; M. Ishida, S. Konda, T. Sasaki and T. Ishikawa: ibid.

Simulation of Corrosion Inhibition of Reinforced Concrete Members by Steel Fibers; T. Notoya, A. Keyvani Someh and N. Saeki: The Winter Meeting of The Hokkaido Secs. of Jpn. Inst. Metals, Jan. 1997.

Behavior of Water in the Surface Layers Formed on Copper in Corrosive Gas Environments; T. Sasaki, T. Itoh, J. Itoh and T. Ishikawa: The 64th Annual Meeting of Electrochem. Soc. Jpn., Yokohama, March, 1997.

IR-RAS Spectra of a Water Layer Formed on Metal Surfaces in Humid Atmosphere; T. Sasaki, J. Itoh and T. Ishikawa: Corrosion '97 of Jpn. Soc. Corros. Eng., Tokyo, May 1997.

Calculation of IR-RAS Spectra of a Thin Layer Formed on Metals from Transmission Spectra; J Itoh, T. Sasaki and T. Ishikawa: ibid.

Inhibition of Hydrogen Evolution with Chromium Compounds on Galvanized Steel Fibers in Concrete; A. Keyvani Someh, N. Saeki and T. Notoya: The 51st Cement Technology Meeting, Tokyo, May, 1997.

Molten Salt Treatments for Recovery of Al from Dross of Al Casting; M. Amemiya, M. Ueda, T. Sasaki and T. Ishikawa: The Summer Joint Meeting of the Hokkaido Secs. of Jpn, Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July, 1997.

Electrolysis and Cell Reaction in a Molten Salt System; T. Ishikawa: ibid.

Localized Corrosion Cases in Copper Tubes for Air-conditioning Units and Their Prevention;T. Notoya: The Summer Joint Meeting of The Hokkaido Secs. of Jpn, Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July, 1997.

Corrosion Inhibition of Newly-Developed Benzotriazole Derivatives for Copper in Sodium Chloride Solutions; T. Notoya, N. Sugii and T. Yamauchi: The 17th Meeting of Jpn. Rust Prevention Association, Tokyo, July, 1997.

Electrorefining of Aluminum Containing Fe-, Mg- and Si-Components; M. Ueda, S.Konda, T. Sasaki and T. Ishikawa: The 5th Internatinal Symposium on Molten Salt Chemistry and Technology, Dresden, Aug., 1997.

In situ IR-RAS Investigation of Water in the Layer Formed on Copper in a Corrosive Gas Environment; J. Itoh, T. Itoh, T. Sasaki and T. Ishikawa: 1997 Joint Int. Meeting - the 192nd Meeting of The Electrochem. Soc. Inc. and the 48th Annual Meeting of the Int. Soc. Electrochem.-, Paris, Aug., 1997.

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: ibid.

An explanation for the Solubility of Benzotriazole Related Corrosion Inhibitors; T. Notoya, H. Tamura, S. Yamamuro, T. Yamauchi and N. Sugii: The 1997 Summer Meeting of the Hokkaido Section of Jpn. Chem. Soc., Kitami, Aug., 1997.

Corrosion of Steel Fiber Reinforced Concrete; A. Keyvani Someh, N. Saeki and T. Notoya: Fourth CANMET/ACI International Conference on Durability of Concrete., Sydney, Australia, Aug., 1997.

Corrosion Protection Shield of Steel Bars, Due to Steel Fibers in Concrete; A. Keyvani Someh, N. Saeki and T. Notoya: Proc. Third CANMET/ACI International Conference, Ackland, New Zealand, Aug., 1997.

Cathodic Reduction Behavior of Dissolved Oxidants on Corroding Surface - Apparatus and Applications-; H. Imai, T. Sasaki and T. Ishikawa: The 44th Discussion Meeting of Jpn. Soc. Corros. Eng., Sendai, Sep. 1997.

Effect of NaCl on Corrosion Layers Initially Formed on Iron in a Gaseous

Corrosion Environment; T. Miyano, T. Sasaki and T. Ishikawa: ibid.

An *in situ* Measurement of Surface Layers Formed on Pure Iron in Corrosive Gas Environments; T. Miyano, T. Sasaki and T. Ishikawa: The 121st Annual Meeting of Jpn. Inst. Metals., Sendai, Sep., 1997.

Recent Features of Ant's Nest Corrosion in Copper Tubes; T. Notoya: The 44th Meeting of Materials and Environment, Sendai, Sept., 1997.

Corrosion Products on Metal Surfaces as Analyzed by *in situ* Simultaneous Measurement with FTIR and QCM; J. Itoh, T. Sasaki, M. Seo and T. Ishikawa: ibid.

Recovery of Aluminum from Aluminum Dross by Using Molten Salt; M. Amemiya, M. Ueda, T. Sasaki and T. Ishikawa: The 97 Fall Meeting of Electrochem. Soc. Jpn., Tokyo, Sep., 1997.

Electrorefining of Aluminum in a Novel Molten Salt; T. Ishikawa: ibid.

Corrosion Inhibition of Copper by Carboxybenzotriazole Derivatives; T. Notoya, N. Sugii and T. Yamauchi:The73rd Fall Meeting of Jpn. Chem. Soc., Morioka, Sept., 1997.

Performance of Chlorine Electrode with an Inclined Axis in an Al-Cl_2 Chemical Cell in Molten Salt System; K. Imasawa, M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: The 29th Meeting of Molten Salt Chemistry, Nov., 1997.

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

Recent "Ant's Nest" Localized Corrosion Cases in Copper Tubes; T. Notoya and K. Kawano: The 37th Meeting of Japan Copper and Brass Research Association, Osaka, Nov., 1997.

Localized "Ant's Nest" Corrosion in Copper Tubes; T. Notoya: Corrosion & Prevention '97, Brisbane, Australia, Nov., 1997.

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Our research activities are in characterization and evaluation of surface properties, surface reactions, surface compositions, and surface morphologies of materials.

The research programs in our laboratory are:

(1) 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 preliminary concentration of trace lithium in natural environments. From a kinetic model analysis of the incorporation of Li into the oxide, it was found that there are two stages of incorporation: an initial period where the incorporation rate decreases steadily due to increasing backward reaction between increasing reaction products and a latter period where the backward reaction rate becomes constant and the first order kinetics with respect to the Li ion concentration is obeyed.

(2) Modeling and characterization of ion exchange properties of the surface of metal oxide particles as corrosion products, battery materials, and soil components.

The fine metal oxide particle/water systems are important in relation to many industrial and natural environmental processes. The acid-base, charge, and ion adsorption characteristics of metal oxides were evaluated by modeling, and it was shown that these characteristics can be explained with the electronegativity of oxides defined by Sanderson. The Co(II) ion adsorption properties of metal oxides are also investigated.

(3) Dissolution of magnetite in chelating agent solutions.

The structural materials of cooling system of (nuclear) power plants are covered with metal oxides (magnetite and others) 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 magnetite in EDTA solutions was modeled, and the effects of pH and oxyen were analyzed. It was found that the effect of pH is due to the pH dependencies of both the concentration of EDTA species and the transfer of lattice oxide ions by proton attack. In the presence of oxygen, the dissolution rate decreases, and this effect was suggested to be due to the loss of dissolved Fe(II)-EDTA chelate by oxygenation, as Fe(II)-EDTA can dissolve magnetite further without O_2.

(4) Initial stage of the high temperature oxidation of Fe-Cr and Fe-Ni-Cr alloys.

There are many works on the high temperature oxidation of Fe-Cr and Fe-Ni-Cr alloys. Many of them concerned with the long time oxidation and the number of the work on the initial oxidation is limited. Study on initial oxidation is important since it may give a information about the oxidation at much longer time and a useful information about operation of stainless steel production, especially descaling and annealing processes. In this work thin films grown on Fe-Cr alloys oxidized in 1 atm of oxidizing gas for 0 to 300 s at 1273 K were analyzed with several methods (TLXRD, XPS, AES-SAM, FTIR-RAS, and FE-SEM) sensitive to the surface properties. Effect of atmosphere, temperature, impurity metal on initial oxidation have been made to clear.

(5) Breakaway oxidation of Type 430 stainless steel.

Breakaway oxidation is a type of abnormal oxidation frequently observed on Fe base alloys at high temperature especially in atmosphere containing water vapor. To explain the origin of the phenomenon and the effect of water vapor on it, XRD method was mainly employed and the following results were obtained. (1) Breakaway oxidation occurred when the film thickness attained a critical thickness which is different with atmosphere. (2) Breakage of the initially grown protective oxide film initiated before breakaway oxidation but broken part was cured itself. (3) Water vapor might affect the self-during action of protective oxide film and shorten the period of breakaway to occur.

(6) Thermal oxidation of Ti covered with metals and investigation of photoelectrochemical properties of the oxides.

TiO_2 are well known as its photo sensitizing properties. As a result, it will be a candidate for solar cell, but larger bandgap energy make it unsuitable. In this study, composite oxides of Ti and M (M=W, Ta, Mo, Ni, Zn, and Cr) were prepared by thermal oxidation of Ti covered with metals as above and the photoelectrochemical response was measured. It was found that composite oxides containing W, Ta and Zn show higher anodic photocurrents than pure TiO_2.

Presentations

An XRD Study of the Oxide Properties Formed on Type 304 Stainless Steel at 1273 K before and after Breakaway; T. Saito, I. Saeki, H. Konno, and R. Furuichi: The Joint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn, Surf. Finish. Soc.. Jpn, and Jpn. Soc. Corros. Eng., Sapporo, Jan, 1997.

Modeling and Evaluation of Ion-Exchange Properties of Surfaces of Metal Oxide Particles; K. Mita, H. Tamura, and R. Furuichi: The 1997 Winter Joint Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1997.

The Photoelectrochemical Properties of Zinc Oxide Electrode Fabricated on Titanium Substrates; I. Saeki, J. Setaka, and R. Furuichi: The 64th Annual Meeting of Electrochem. Soc. Jpn., Yokohama, Mar, 1997.

A Method to Evaluate the Ion-Exchange Properties of Lake and River Sediments; S. Kawamura, F. Terui, and H. Tamura: The 31st Annual Meeting of the Japan Water Environment Society, Sapporo, Mar., 1997.

What Determines the Ion-Exchange Ability of Metal Oxides? -Evaluation by Modeling-; H. Tamura, K. Mita, and R. Furuichi: The 72nd Spring Annual Meeting of Chem. Soc. Jpn., Tokyo, Mar., 1997.

What Determines the Ion-Exchange Ability of Metal Oxides? -Correlation with the Electonegativity-; H. Tamura: The 5th Lilac Seminar Sponsored by the Hokkaido Sec. of the Electochem.Soc. Jpn., Otaki, Jun., 1997.

Detemination of the Surface Hydroxyl Groups on λ -MnO_2 (Manganese Dioxide with Lattice Vacancies) with the Grignard Method; A. Tanaka, H. Tamura, and R. Furuichi: The 1997 Summer Joint Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Kitami, Jul., 1997.

A Comparative Study in the Oxide Film Properties Formed before and after Breakaway on Type 304 Stainless Steel at 1273 K; I. Saeki, T. Saito, R. Furuichi, and H. Konno : The 44th Discussion Meeting of Jpn. Soc. Corros. Eng., Sendai, Sep. 1997.

Ion Adsorption Affinity of Metal Oxides for Preconcentration -Covalent or Ionic Bond?-; H. Tamura and R. Furuichi: The 46th Annual Meeting of Jpn. Soc. for Anal. Chem., Tokyo, Oct., 1997.

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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, migration of noble metal fission products in UO_2, thermal properties of cesium uranates, and radioactive waste management.

Current research topics include:

(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 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 the 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 x 10^{-11} m^2s^{-1} was obtained from the He concentration profiles. In addition, the amount of helium was found to be 0.5 x 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.

(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.

(6) Relationships between kinetics of hydrogen absorption and hydrogen concentration profiles of Ti and Zr by electrolysis were investigated by electrochemical, chemical and other conventional techniques. 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. A 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.

(7) Processes of passivation and localized corrosion of metals were studied with a 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 was invited to the first international new science symposium at Ajoh university Korea in May 2-5, 1997, and the meeting of the anomalous reaction mechanism works between metal and hydrogen at Moscow university in May 25-June 4, 1997. He attended the Intersociety engineering conference on energy conversion at Hawaii in July 27-August 1, 1997.

Reserch.Associate. Mr. T. Kozaki attended the 1997 Material Research Society

Fall Meeting on Scientific Basis for Nuclear Waste Management XXI, held in September-October, Davos, Switzerland and presented the paper entitled "The dependence of the diffusion coefficients of ^{3}H and Cs on grain size in compacted montmorillonite".He attended the Sixth International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, held in October, Sendai, Japan, and presented the paper entitled "Activation energy for diffusion of chloride ions in compacted montmorillonite".

M.Samadfam, S.Sato, and H.Ohashi attended the International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, held in October, Sendai, Japan.

Foreign researchers visited the Nuclear Material System Laboratory in April include Dr. C. A. Degueldre from Paul Scherrer Institute, Switzerland, and T. T. Vandergraaf from Whiteshell Laboratory, AECL Research, Canada.

Presentations

Chemistry and Engineering of Actinide Elements (Invited lecture); Hiroshi Ohashi: The Research Committee on The Research Institutes for Application of Radioisotopes and Radiation in Rokkasyo Mura, Japan Atomic Industrial Forum, Inc., Tokyo, January, 1997.

Activation Energies for Diffusion of Cations in Compacted Sodiummontmorillonite; Tamotsu Kozaki, Atsushi Fujishima, Hiroki Sato, Nobuhiko Saito, Seichi Sato, Hiroshi Ohashi: Jitsuya Takada and Hirotake Moriyama, the Scientific Meeting of the Research Reactor Institute, Kyoto University, Kumatori-cho, January, 1997.

Energy, Resource and Eevironment (Invited lecture); Hiroshi Ohashi: The 34th Hokkaido High School Education Research Meeting, Sapporo January 1997.

Effect of Oxidation of Pyrite on Corrosion Behavior of Iron Overpack in Compacted Bentonite; Hideki Kawabe, Tamotsu Kozaki, Seichi Sato and Hiroshi Ohashi: The Winter Joint Meeting of The Hokkaido Secs. of Chem. Soc. Jpn., and Jpn. Soc. Anal. Chem, Sapporo, February 1997.

Properties of Plutonium and Design of Reactor Core (4); Properties of MOX Fuels, Hiroshi Ohashi and Kousaku Fukuda: The Joint Meeting of The University of Tokyo Yayoi Research Committee and The Research Committee on Advanced Nuclear Fuels and Reactor Materials, "Present Status and Problems of Application of Plutonium Mixed Oxide Fuels" , Tokyo March, 1997.

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Migration Behavior of Cations in Na/Ca-Montmorillonite (II) -Activation Energy for Diffusion of Cesium Ions-; Hiroki Sato, Nobuhiko Saito, Tamotsu Kozaki, Seichi Sato and Hiroshi Ohashi: The 1997 Fall Meeting of The Atomic Energy Society of Japan, Naha, October, 1997.

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

Current topics on research are as follows :

(1) 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 aqueous solutions containing iodide ions in order to evaluate the structural changes of iodine adlayer. The potential of zero charge (pzc) of gold electrode evaluated by the laser beam deflection method was consistent with that previously obtained by piezoelectric technique.

Moreover, at the higher potentials far from pzc, the absolute value of the derivative of surface energy with electrode potential, $|\partial \gamma^s/\partial E|$, which should be equal to the surface charge density, $|Q_m|$, decreased with increasing the potential. On the other hand, the cyclic voltammogram of the gold electrode indicated that the surface charge density, Q_m, with positive sign increased with increasing potential. This contradiction may be ascribed to the structural change or phase change of iodine adlayer at the higher potentials far from pzc.

(2) In-Situ Nanoindentation of Single Crystal Iron (100) Surface Passivated in pH 8.4 Boric-Borate Solution

A local breakdown of passive film on metal leads eventually to pitting corrosion of the metal itself. The mechanical property of local site of passive surface would be closely related to the breakdown. However, there were few studies of mechanical property of passive surface reported so far. Recently, the nano-indentation technique combined with an atomic force microscope (AFM) has been developed to evaluate the mechanical property of a local site of a material surface. The in-situ nanoindentation of a single crystal iron (100) surface passivated in pH 8.4 boric-borate solution is being conducted to examine the mechanical property of a passive surface with relation to the local breakdown.

(3) Measurement of Membrane Potential of MnO_2 Prepared on Platinum Net Electrode with Electrosynthesis

MnO_2 was anodically deposited on a platinum mesh electrode in Na_2SO_4 -

H_2SO_4 aqueous solution containing $MnSO_4$. The XRD and laser Raman spectroscopy showed that MnO_2 contains crystalline γ-MnO_2. The SEM observation indicated that the surface morphology of MnO_2 is fibriform. The ion-selective permeability of MnO_2 was evaluated from the measurement of the membrane potential. It was found that MnO_2 is cation selective for KCl, NaCl, KNO_3 and Na_2SO_4 aqueous solutions. On the other hand, MnO_2 is anion selective for KOH, NaOH and LiOH aqueous solutions.

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

A Scanning Electrochemical Microscope (SECM) was applied to evaluate the heterogeneity of passive films formed on polycrystalline iron and titanium electrodes which were passivated in deaerated pH 8.4 borate solution. The current images were measured with a tip-generation/substrate-collection (TG/SC) mode in deaerated pH 8.4 borate solution containing $[Fe(CN)_6]^{4-}$ as a mediator. The probe current images of passive films on polycrystalline metals depended strongly on the grain orientation. In the case of passive films on polycrystalline iron, the probe current increased in the order of grain orientation, $\{100\} \ll \{111\} < \{110\}$. This difference in probe current for passive films on polycrystalline iron electrode may be ascribed to the difference in thickness of passive films since $[Fe(CN)_6]^{3-}$ reduction proceeds with an electron tunneling through the films.

(5) Electroluminescence from Porous Silicon Layer during Anodic Oxidation

Electroluminescence (EL) from a porous silicon layer (PSL) during anodic oxidation up to 500 V (SHE) under galvanostatic conditions in 0.1 M KNO_3 ethylene glycol solution was measured in relation to the anodic oxidation mechanism of PSL. The PSL was prepared on a single crystal p-type Si (100) wafer with an electrochemical etching in 22.6 wt% HF ethanol solution. The TEM image and FT-IR spectrum have indicated that the PSL as prepared consists of Si particles with sizes of 2 nm - 5 nm and the Si particles are covered with silicon hydrides, SiH_x. At the initial stage of anodic oxidation of the PSL, SiH_x

on Si particles is firstly oxidized to elemental Si and simultaneously an EL with a peak of 760 nm is emitted from the PSL. At the subsequent stage of anodic oxidation, Si particles are oxidized to form a SiO_2 film and simultaneously an EL with two peaks of 530 nm and 650 nm is emitted from the PSL. The EL mechanism of the PSL during anodic oxidation was explained in terms of the electronic band models of the Si | SiHx | solution and Si | SiO_2 | solution systems.

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

Long term stability of the anodic oxide film formed on titanium under the deaerated aqueous environment is examined by using immersion potential and impedance monitoring technique. Mechanically polished Ti and anodized Ti specimens were put in small electrochemical cells and left in deaerated borate, carbonate and bentonite-contacting solutions at 25 and 80 ℃ for a few month. In most cases an immersion potential shifted to positive direction, and capacitance decreased during long term immersion, indicating that the oxide layer grows on Ti even in deaerated aqueous envirnoment. The electronic property of the anodic oxide film formed in bentonite-contacting solution is, however, different from that in the other solutions.

(7) Electrochemical Analysis of the Double Zincate Process of Aluminum Alloys

Al and Al alloy surfaces were observed using AFM technique before and after zincate treatments. The Al surface after Zn stripping was composed from mountain-like structure and plane surface. The former was covered by Zn particle deposition before stripping, and initiates new Zn deposition at 2nd zincate process. The latter surface shows dissolution pattern in sub-micron scale which was also observed for Al surface after dissolution treatment in conc. NaOH solution. It is proposed from XPS analysis that the plane surface is covered by Al oxide and Al hydroxide layer which is thicker than that on the surface of mountain-like structure.

(8) Monitoring of Hydrogen Absorption into Ti using Resistometry

Hydrogen absorption into Ti is an important issue because it leads rupture of materials. Electric resistance of Ti foil with 50 μm thickness was measured during galvanostatic cathodic polarization for hydrogen absorption. The resistance increases accompanying with hydrogen absorption into Ti.When cathodic current density is smaller than a critical value, increase of resistance shows saturation, indicating that hydrogen concentration reaches some saturation value. When cathodic current density is larger than the critical value, the resistance increases continuously until hydrogen fracturing. Growth of the anodic oxide film on Ti also affected the hydrogen absorption behavior.

Other Activities

In August and September, Prof. M. Seo and Mr. K. Ueno (Ph.D. Student) visited Prof. R. Winand, Materials Science and Engineering Department, Faculty of Applied Sciences, Universite Libre de Bruxelles, Belgium and then attended the Joint International Meeting of ECS and ISE held in Paris, France to present the two papers entitled " Corrosion Kinetics of Iron Thin Film in Deaerated Phosphate Solutions by an EQCM" and " Piezoelectric Detection of Changes in Surface Energy of Iron Electrode". Afterward, Prof. M. Seo and Dr. M. Sakairi visited Prof. R. Oltra, Laboratoire de Recherches sur la Raètivitè des Solides, Universite de Bourgogne, France.

In October, Prof. M. Seo was invited to Korea for one week by Prof. Su-Il Pyun, Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejon and presented the Seminar entitled " An EQCM Study on Corrosion Kinetics of Iron Thin Films" at KAIST and Korea Atomic Energy Research Institute (KAERI). Afterward, Prof. M. Seo visited the Pohang Iron and Steel Company, Kwang Yang, Korea. Moreover, Dr. Achim Walter Hassel, Institute for Physical Chemistry and Electrochemistry II, Heinrich-Heine-University Düsseldorf, Germany joined this laboratory from October 15 th as a foreign researcher supported by the Japan Society for the

Promotion of Science to conduct the research on measurement of surface energy images by a scanning piezoelectric method combined with a droplet method.

The following foreign scientists visited this laboratory : Dr. S. Hofmann, National Research Institute for Metals, Tsukuba on January 16 -17, Prof. A. T. Fromhold, Jr., Department of Physics, Auburn University, Alabama, USA on March 10 - 13, Mr. M. S. El-Deab, Faculty of Science, University of Cairo, Egypt, Mr. M. Shahabi, Chemical Research Center, Jahad Daneshgahi Institute, Sharif University of Technology, Iran, Ms. L. V. Mercado, Iztapalapa Metropolitan Autonomous University, Mexico on October 3, Prof. G. Hultquist, Division of Corrosion Science, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm, Sweden on November 10 -14, and Dr. J.-L. Delplancke, Department of Metallurgy-Electrochemistry, Universite Libre de Bruxelles, Belgium on November 17.

Presentations

Application of Scanning Electrochemical Microscope to Anodic Oxide Films on Iron and Titanium ; K. Fushimi and M. Seo : The 1997 Joint Meeting of Hokkaido Sec. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Corros. Eng., Sapporo, Jan., 1997.

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pH Dependence of Corrosion Rate of Electroplated Iron Thin Film in Deaerated Phosphate Solutions ; M. Kurosaki and M. Seo : ibid.

Changes in Surface Morphology of Carbon Steel and Pure Iron due to Corrosion in Deaerated Carbonate Solutions ; K. Suzuki, K. Fushimi, K. Azumi and M. Seo : ibid.

Surface Pretreatment Effects of Al Alloy Surface on Zn Deposition in Zincate Process ; Y. Fujishige, K. Azumi and M. Seo : ibid.

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Stability of Anodic Oxide Film on Ti in Non-oxidative Environment; K. Azumi, N. Yasui and M. Seo: ibid.

Applications of Scanning Electrochemical Microscope to Corrosion Systems; K. Fushimi: The 4th Exchanging Meeting for Young Researchers of Hokkaido Sec. of Electrochem. Soc. Jpn., Ohtaki, June, 1997

Computer Application in the Chemistry Laboratory; K. Azumi: The 37th Aurora Seminar of the Hokkaido Sec. of Catal. Soc. Jpn. and Chem. Soc. Jpn., Nishi-Okkoppe, August, 1997

Piezoelectric Detection of Changes in Surface Energy of Iron Electrode; K. Ueno, and M. Seo: The Joint International Meeting of the Electrochemical Society and the International Society of Electrochemistry, Paris, France, Sept., 1997.

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Analysis of Surface Reaction Distribution of Electrode by a Scanning Electrochemical Microscope; M. Seo and K. Fushimi: Symposium on " New Analytical Methods of Surface and Interface", Jpn. Inst. Metals,Tokyo,Dec.,1997.

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We accepted visitors from abroad, Professor W. Wu from Institute of Corrosion and Protection of Metals, The Chinese Academy of Science in China, Professors D. J. Young and B. Glesson from University of New South Wales, in Australia, Professor J. H. Yoon from Changwon National University in Korea, accompanied with his students. Professor B. Hu from University of Science and Technology Beizing in China, Mrs. X. F. Ren from China International Culture Exchange Center, and Mr. H. Xia from General Research Institute for Non-

Ferrous Metals in China.

Assoc. Prof. Yu Jinming stayed as a visiting researcher from Institute of Corrosion and Protection of Metals Academia Sinica, China

Professor Narita attended Golden Research Conference held at NH. USA, in July , and presented a paper entitled " High Temperature Sulfidation of Metals and Alloys " , and he visited University of Pittsburg in USA and Chongwon University in Korea. Professor Narita was invited by the China International Culture Exchange Center and visited University of science and Technology Beizing, General Research Institute for Non-Ferrous Metals, Northwest Institute for Non-Ferrous Metal Research, Central Iron and Steel Research Insitute in China. Professor Narita visited University of New South Wales in Australia along with Mr. Taumi and Mr. Hata.

The research activities of the laboratory are directed to an understanding of high temperature corrosion mechanisms of superalloy, 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) Corrosion Resistant Aluminum Cast Iron

In order to develop a low cost and corrosion resistant material, cast iron containing high content of aluminum was made, and its properties were evaluated.

(10) 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.

(11) 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.

Presentations

Effect of Bonding Layer Thickness on Fracture Strength of Silicon Nitride Joints with Ni-Cu-Ti Solder ; S. Hata and T. Narita: The 120th Annual Meeting of Jpn. Inst. Metals., Tokyo, Mar. ,1997.

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Nitrogen; Y. Mizuno, K. Ohsasa and T. Narita: The 121th Annual Meeting of Jpn. Inst. Metals., Sendai, Sept. ,1997.

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Effect of Heat Treatment on the Hardness and the Structure of Sn-Bi Eutectic Solder Alloy; J. Hu, H. Tanaka, M. Taguchi and T. Narita: The 121th Annual Meeting of Jpn. Inst. Metals., Sendai, Sept.,1997.

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Foreign Researcher

D. A. Armijo

Students

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H.Houzumi, Y. Ohira, G.Ochiai, K. Watanabe,
Y. Kawamoto, T. Kikuchi, J. Kuchino, and K. Yamauchi

In April, Ms. Chu passed the entrance exam. of DC, and started her life as a DC student. Mr. D. Aguilar Armijo joined the laboratory as a foreign researcher from Honduras University in July.

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 and AFM abrasion.

Current topics on research are in the following:

(1) Local copper deposition on aluminum by AFM abrasion

Aluminum specimen covered with barrier type anodic oxide films was immersed in Cu^{2+} ion containing solutions, and abraded with a probe of atomic force microscope (AFM) to remove the oxide film. Time variation in the depth of hollow at the abraded area was followed by the in situ AFM measurement. The hollow depth increased linearly with increasing the number of abrasion scanning, and decreased with time after abrasion by the deposition of Cu at the abraded area.

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

Aluminum specimen covered with porous anodic oxide films was immersed in Ni-P electroless plating solution, and irradiated with a pulsed YAG laser through a lens and quartz window to remove the oxide film locally. The specimen was transferred into a new Ni-P electroless plating solution at high temperature to deposit Ni-P at the laser-irradiated area. The electroless deposition of Ni-P was affected considerably by the concentration of Pb^{2+} ions in the electroless plating solution and temperature. With increasing Pb^{2+} ion concentration, the Ni-P deposition rate decreased but space selectivity of deposition increased. The deposit showed 9 - 11 at. % phosphorus content and amorphous structure.

(3) Surface patterning of aluminum with laser irradiation and Ni electrodeposition.

Aluminum specimen covered with porous anodic oxide films was immersed in Ni^{2+} ion containing solutions, and then irradiated with a pulsed YAG laser through a convex lens before cathodic polarization. By using a lens with a short focal distance, a fine coil pattern of Ni-deposits with 15 μm line width was obtained on the specimen. A simple circuit board was obtained by sticking the Ni-deposited specimen on an organic insulating board, and by dissolving the metal substrate.

(4) Formation of oxide films on aluminum after destruction of anodic oxide film

with laser irradiation.

Aluminum specimen covered with porous and barrier type anodic oxide films was immersed in neutral borate solutions with or without Cl^- ions, and irradiated with one pulse of laser under anodic polarization. In the solution without Cl^- ions, the kinetics of oxide film formation after laser irradiation followed the inverse logarithmic law, suggesting a film growth theory under high electric field. In the solution with Cl^- ions at concentrations above 10^{-2} M, the rapid decrease in current in the initial stage was followed by an increase through a minimum at 10 - 30 ms, and this suggested a pit formation after film repairing.

(5) Formation of aluminum anodic oxide films with ultra high potential sustaining ability by pore-filling method.

Porous anodic oxide film covered-aluminum specimen was anodized galvanostatically in 0.1 M-boric acid and $5x10^{-5}$ M-KOH solutions to examine the formation and breakdown of anodic oxide film during anodizing. In the both solution, oxide formation occurred at the bottom of pores and the interface between oxide film and the metal substrate. In the boric acid solution, breakdown potential for the porous film covered-specimen was 1,400 V, which was 200 V higher than that for specimen without film, while in KOH solution breakdown potential was not affected by the formation of porous anodic oxide film before anodizing.

(6) 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. Some specimen was heated in air between MOCVD and anodizing. During anodizing, anodic oxide films were formed, which consisted of an outer Al / Ti composite oxide layer and an inner Al_2O_3 layer, and the thickness ratio of the outer layer to the inner layer increased with increasing MOCVD temperature. Heat treatment after MOCVD affected very much the formation of anodic oxide films, causing the formation of a crystalline Al_2O_3

layer with a high electric field sustaining ability. The electric capacitance of the anodic oxide films formed on specimens coated with TiO_2 was higher by 25 - 66 % than that on the specimen without TiO_2 coating.

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

Aluminum specimen was initially coated with ZrO_2 by sol-gel dip-coating in a zirconium alkoxide / ethanol mixture, and then anodized galvanostatically in a neutral borate solution. During anodizing, anodic oxide films were formed, which consisted of an outer Al / Zr composite oxide layer and an inner Al_2O_3 layer. With increasing the number of dipping / heating cycles, n, the capacitance of anodic oxide films increased by 15 % at most below n = 6, but above n = 8, decreased considerably.

(8) Complementary observation of hydroxide film formation on aluminum by SEM, TEM, and AFM.

Electropolished pure aluminum specimen was immersed in doubly distilled water at 40 ℃, to examine how the hydroxide film is formed during immersion by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). In the initial period of immersion, flake-shaped hydroxide were formed on the ridge of scallop-shaped surface, and the hydroxide formed a network structure before three dimensional growth of hydroxide films.

(9) Interfacial reactions between refractory metals and $MoSi_2$.

The interfacial reactions in refractory metal (Ta and Nb)/ $MoSi_2$ systems at high temperatures are being investigated. The aims are to clarify the mechanism of the interfacial reactions and to estimate the maximum application temperature of the systems. In addition, study on suppression of the interfacial reactions is also in progress.

(10) Synthesis of $MoSi_2$-based composites.

A spark plasma sintering method has been applied for the synthesis of fully dense $MoSi_2$-SiC composites. In the sintering, elemental Mo, Si and C powders are usually used for in-situ synthesis of the composites. The most suitable temperature for the synthesis, the sintering behavior and the reaction behavior between elemental constituents have investigated.

(11) Accelerated oxidation of $MoSi_2$-based materials.

In order to clarify the process of accelerated oxidation and pesting, low temperature oxidation of $MoSi_2$-based materials is being investigated. Thermodynamical prediction shows that simultaneous oxidation of Mo and Si is not an intrinsic property of $MoSi_2$. However, the simultaneous oxidation occurrs preferencially at defects such as pores, resulting in pesting. In addition, H_2O vapor in air accelerates occurrence of pesting in porous $MoSi_2$, though it has no influence on the oxidation behavior of fully dense $MoSi_2$.

(12) High temperature oxidation of SiO_2-forming materials.

Oxidation of SiO_2-forming materials such as $MoSi_2$ and SiC at ultra-high temperatures is being investigated. The aim is to clarify the oxidation behavior of the SiO_2-forming materials. Especially, emphasis is the effects of second phase such as additives and reinforcrment materials on the oxidation behavior of SiO_2-forming materials.

Other activities

Prof. Takahashi attended the 1st International Symposium on Aluminium Surface Science and Technology, which was held at Antwerp in Bergium on 11 - 15 of May, and presented a paper entitled " Surface Patterning of Aluminum with Laser Irradiation and Electrochemistry". After the symposium he visited Prof. H. Terryn at Free University, Brussels and Prof. R. Oltra at Brugoneua University to discuss the anodic oxidation of aluminum. Dr. Sakairi attended the Symposium on Passivity and Its Breakdown, co-sponsored by the Elctrochemical Society and

International Sciety of Electrochemisty at Paris on 1 - 5 of September, and presented a paper entitled "Reformation of Anodic Oxide Films on Aluminum after Destruction by Pulsed Nd-YAG Laser Irradiation". After the symposium, he visited Prof. R. Oltra at Brugoneua University to discuss the destruction of oxide films by laser irradiation. Assoc. Prof. Kurokawa attended the First International Symposium on Applied Plasma Science, which was held at Los Angeles in U. S. A. on 22-26 of September, and presented a paper entitled "In-situ synthesis of fully dense $MoSi_2$-SiC composites by spark plasma sintering".

Foreign researchers visited the IMSA- Laboratory are Dr. G. Brown, Keio University on 9 -13 of July, Prof. S. Duan, University of Science and Technology, Beijin, on 28 - 31 of July, Prof. J. H. Yoon, Chanwon National University, Korea, on 30th of July, Prof. D. J. Young and Dr. B. Gleeson, University of New South Wales, Australia, on 10th of September, and Profs. G. C. Wood and G. E. Thompson, UMIST, England, on 17 -19 of November.

Presentations

AFM Observation of Growth of Anodic Oxide Films on Aluminum; F. Takashima, M. Sakairi, H. Takahashi, and K. Abe: The joint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc., Jpn., and Jpn. Soc. Corros. Eng., Sapporo, Jan., 1997

Anodizing of Aluminum Covered with MOCVD-TiO_2 Film. - Effects of Temperatures during MOCVD and Heat Treatment on the Formation of Anodic Oxide Films -; H. Kamada, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, and S. Yamaguchi, ibid.

Fabrication and Oxidation of Mo-Si-C Composites; M. Ube, K. Kurokawa and H. Takahashi: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July, 1997.

Anodic Oxidation of Aluminum in KOH solution; H. Shimada, M. Sakairi, K. Shigyo, M. Seo, H. Takahashi: The Winter Joint Meeting of The Hokkaido

Secs. of Chem. Soc. Jpn., and Jpn. Soc. Anal. Chem., Sapporo, Feb., 1997.

Interfacial Reaction and Bonding between $MoSi_2$ and Graphite; K. Kurokawa, T. Horibe and H. Takahashi: 1997 Symposium on Advanced Research of Energy Technology, Sapporo, Mar., 1997.

Chemical Compatibility of $MoSi_2$ with Refractory Metals; K. Kurokawa: The 4th Meeting of Inst. of Applied Plasma Sci., Nagoya, Mar., 1997.

Influence of BN on High Temperature Oxidation Behavior of Nitride-Based Ceramics; K. Kurokawa, M. Nonaka, H. Takahashi, and M. Ueki: The 120th Annual Meeting of The Institute of Metals, Jpn.: Tokyo, Mar., 1997.

High Temperature Oxidation Behavior of Sintered Bodies of Mo-Si-C Systems; K. Kurokawa, M. Ube and H. Takahashi: ibid.

Anodic Oxidation of Aluminum in diluted KOH Solutions; H. Shimada, M. Sakairi, K. Shigyo, M. Seo, H. Takahashi: The 95th Annual Meeting of Sur. Finish. Soc. Jpn., Tokyo, Mar., 1997.

In Situ AFM Observation of the Formation of Anodic Oxide Films on Aluminum; F. Takashima, M. Sakairi, H. Takahashi, and K. Abe: ibid.

Surface Functionalization of Aluminum by Anodizing (Invited Lecture); H. Takahashi: ibid.

Destruciton of Thick Anodic Oxide Films on Aluminum with Laser Irradiation and Local Ni-Plating at the Laser-Irradiated Area; M. Sakairi, Z. Kato, S. Chu, and H. Takahashi: '97 Annual Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1997.

Effects of Heat Treatment on the Formation of Al-Ti composite Oxide Films by CVD and Anodizing; H. Kamada, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, and S. Yamaguchi: ibid.

Surface Patterning of Aluminium with Laser Irradiation and Electrochemistry; H. Takahashi, J. Wakabayashi, K. Nukui, M. Sakairi, M. Seo, Y. Matsumi, and M. Kawasaki: The 1st Intern. Symp. on Aluminium Surface Sci. and Technology, Antwerp, Belugium, May, 1997.

Oxide Film Formation on Aluminum after Breakdown by Laser Irradiation; H. Takahashi, Y. Ohira, M. Sakairi: Seminar at Dijon University, Dijon, France, May, 1997.

Local Surface Modification with Laser Irradiation (Invited Lecture); H.Takahashi, M. Sakairi, K. Nukui, J. Wakabayashi, and Z. Kato: Seminar on New Technology of Surface Modification of Aluminium and Its Alloys and Their Composite Materials.(Sponsored by Light Metal Inst. Jpn.), Jun., 1997.

Front of Anodizing of Aluminum. - Functionalization of Surface - (Invited Lecture); H. Takahashi: Seminar of Kansai Branch of Jpn. Sci., Color Material, Osaka, Jun., 1997.

Accelerated of $MoSi_2$ during Accelerated Oxidation; H. Houzumi, K. Kurokawa and H. Takahashi: The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July, 1997.

Interfacial Reactions between Refractory Metals and $MoSi_2$ and the Interface Structures; G. Ochiai, K. Kurokawa and H. Takahashi: ibid.

Self Repairing of Anodic Oxide Films Destructed by Laser Irradiation; Y. Ohira, M. Skairi, and H. Takahashi: ibid.

Formation of Al-Valve Metal Composite Oxide Films by CVD / Anodizing; H. Kamada, M. Sakairi, M. Seo, H. Takahashi, K. Takahiro, S. Nagata, and S. Yamaguchi: The 96th Annual Meeting of Sur. Finish. Soc. Jpn., Tokyo, Sep., 1997.

Local Deposition of Ni-P on Aluminum with Laser Irradiation and Electroless plating; S. Chu, M. Sakairi, and H. Takahashi: The Fall Meeting of Electrochem. Soc. Jpn., Tokyo, Sep., 1997.

In Situ AFM Observation of Aluminum Surface and Micro Structure Fabrication with AFM Probe; F. Takashima, M. Sakairi, and H. Takahashi: ibid.

In-Situ Synthesis of Fully Dense $MoSi_2$-SiC Composites by Spark Plasma Sintering; K. Kurokawa, M. Ube and H. Takahashi: The 1st Inter'l Sympo. on Applied Plasma Sci., Los Angeles, U. S. A., Sep., 1997.

Changes in Surface and Inside of $MoSi_2$ during Accelerated Oxidation; H. Houzumi, K. Kurokawa and H. Takahashi: The 121st Annual Meeting of The Institute of Metals, Jpn.: Sendai, Sep., 1997.

Interface Reactions between Refractory Metals and $MoSi_2$; G. Ochiai, K.

Kurokawa and H. Takahashi: ibid.

In-Situ Synthesis of $MoSi_2$-SiC Composites by A Spark Plasma Sintering Method; K. Kurokawa: The 2nd Seminar on Spark Plasma Sintering, Tazawako, Sep.,1997.

Mechanism of Aluminum Oxide Formation after Destruction by Laser Irradiation: Y. Ohira, M. Sakairi, and H. Takahashi: The 44th Discussion Meeting of Jpn. Soc. Corros. Eng., Sendai, Sep., 1997

Local Surface Modification of Aluminum by Laser Irradiation, AFM Probe Abrasion and Electrochemistry; H. Takahashi, S. Chu, F. Takashima, and M. Sakairi: Seminar at The Institute of Material Research, Tohoku University, Sendai, Nov., 1997

DENTAL MATERIALS AND ENGINEERING LABORATORY

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The research activities cover (1)the development, evaluation and application of dental/biomaterials, (2)the development of methods and equipments for fabrication of materials and prostheses and (3)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, engineering fields and performed in collaboration with clinical departments including prosthodontics, operative dentistry, orthodontics.

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

(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 metals were implanted. The dissolution of implanted metals and inflammation of tissues were observed by elemental mapping image obtained by XSAM.

Other activities

Prof. Maud BERGMAN of Institute of Dental Materials Science, Umeå University (SWEDEN) stayed for Feb.2-19 under the subject of "development of new dental materials and their clinical application in high aged society" with the grant of Hokkaido University Exchange Program. She made a presentation on "Dental all-ceramic restorations" and gave students a lecture in dental school. Prof. Bo BERGMAN of Department of Prosthodontics, Umea University visited together and gave a presentation on "Prosthodontic education and practice in Sweden with special emphasis on special training". The collaboration on application of Ti, ZrO_2 for dentistry, research on side effects and other subjects is going on.

Prof. Tae-Sung BAE of Department of Dental Materials, Chonbuk National University (KOREA) stayed for Feb.24-March 4 for the study of dental ceramics and resin.

Prof. Arne OLSEN of Department of Physics, University of Oslo (Norway) visited on Aug. 20-21 and gave a lecture on "Electron Microscopy of Dental Ga Alloys and its Related Crystalline Phases".

Presentations

Mechanical Properties and Estheticity of New FRP Orthodontic Wire; T. Imai, M. Kobayashi, F. Watari, S.Yamagata, K. Nagayama and S.Nakamura: The 75th IADR, Orlando, March, 1997.

Functions of New Microscopes such as Natural-SEM and X-ray Analytical Microscope; F. Watari, M. Uo: Hokkaido Shigakukai, Sapporo, April, 1997

Grafting of Methyl Methacrylate onto Collagen Using Ferric Chloride-N-Phenylglycine; S. Kondo,S. Ohkawa,M. Uo,T. Sugawara and F.Watari:The 75th International Association for Dental Research,Orlando, Florida, March,1997.

Fracture Tougheness of PMMA-Based Heat-Cured Denture Base Materials Modified with Macromonomer; S. Kondo, S. Ohkawa, M. Uo,T. Sugawara and F. Watari: The 29th Jap. soc. Dent. Mater. and Dev., Tokyo, April, 1997.

Mechanical Properties and Processing Shrinkage of PMMA-MMA-Based Denture Base Resins Modified with Expansible Spherical
Filler; S. Kondo, S. Ohkawa, M. Uo, T. Sugawara and F. Watari: The 30th

Jap. soc. Dent. Mater.and Dev.,Fukuoka, Sept., 1997.

AgCl-LiF-KHF_2 Fluxes for the Soldering of Titanium; S. Ohkawa, K. Ishii, S. Kondo, M. Uo, T. Sugawara, F. Watari: Third International Congress on Dental Materials, Hawaii, Nov.4-8, 220, 1997.

Preparation of Glass-Ceramics by Sol-Gel Process and Dental Applications; M. Uo, T. Sugawara, S. Ohkawa, S. Kondo, F. Watari: Hokkaido Shigakukai, Sapporo, April, 1997.

Study on Glass Fillers using Porous Glasses and Gels; M. Uo, T.Sugawara, S. Ohkawa, S. Kondo and F. Watari: The 30th Jap.soc. Dent.Mater.and Dev., Fukuoka, Sept., 1997.

Analysis of Oxide films on Metals (1)
Infrared Reflection Absorption Spectroscopy

Takeshi Sasaki and Tatsuo Ishikawa

Denki Kagaku, **65**, 730-734(1997)

The principle and sensitivity of an *in situ* IR-RAS technique for analysis of corrosion layers on metal surfaces were described together with the included limitation. The results from copper/humid air and copper/humid air containing sulfur dioxide systems, as a example, were presented. (Japanese)

IN SITU SIMULTANEOUS MEASUREMENT WITH IR-RAS AND QCM FOR INVESTIGATION OF CORROSION OF COPPER IN A GASEOUS ENVIRONMENT

J. ITOH, T. SASAKI, M. SEO AND T. ISHIKAWA

Corros. Sci., **39**, 193-197 (1997)

To elucidate the initial corrosion behavior at metal surfaces in corrosive gas environments a method for *in situ* simultaneous measurements using IR-RAS and QCM was developed. The technique was applied to copper in air containing 10 ppm SO_2 and 80% relative humidity and the results were discussed.
(English)

IR-RAS Spectra of Corrosion Products on Copper

Jun Itoh, Takeshi Sasaki and Tatsuo Ishikwa

Zairyo-to-Kankyo, **46**, 777-782(1997)

In situ IR-RAS (Infrared Reflection Absorption Spectroscopy) is a powerful technique for investigation of the initiation of atmospheric corrosion, but the interpretation of the spectra is not always easy, because the band positions and shapes of the IR-RAS spectra possibly change from those of the transmission spectra due to an abnormal dispersion of the refractive indexes of surface layers.

To estimate the band shifts, IR-RAS spectra of corrosion products and related compounds were theoretically calculated by using their optical constants which were derived from the transmission spectra and the Kramas-Kronig analysis. In this procedure a three phase model (air/surface layer/copper) and a four phase model (air/water layer/ corrosion product layer/copper) were employed and their results were compared.

The band of IR-RAS spectra shifted to higher wavenumber region and the values of $CuSO_4 \cdot H_2O$, $CuSO_4$, Na_2SO_4, and Chevruel's salt ($Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$) were 10, 64, 20, and 18 cm^{-1}, respectively. A spectrum obtained on copper in air containing 10 ppm SO_2 and 80% relative humidity of water was analyzed based on the calculated IR-RAS spectra. (Japanese)

Tunneling Spectroscopy of Passive Films on Iron and Titanium

K. Azumi, K. Araki and M. Seo

J. Electroanal. Chem. and Interfacial Chem., **427**, No.4, 15-21 (1997)

In-situ electrochemical tunneling spectroscopy (TS) was used to investigate the electronic properties of n-type semiconductive passive films formed on metals. The tunneling current, I_T, for Pt, Fe and Ti was measured as a function of distance, Z, bias voltage, ϕ_B, and polarization potential, ϕ_P, respectively. A comparison of I_T - ϕ_B spectra of Pt and passivated metals showed that the tunneling barrier of the latter is dominated by the space charge layer in the passive film under anodic polarization. There were difficulties in measuring TS in the electrochemical system, such as the limitation of a narrow bias scanning range and the polarization effect of the tip electrode (TE) near the surface of the specimen. On the other hand, a wide range of potential scanning was achieved in I_T - ϕ_P measurement because the polarization potential of the TE was kept constant during the ϕ_P scan. In I_T - ϕ_P spectra of the Ti electrode, formation and annihilation of the depletion layer and dielectric breakdown were clearly observed as a function of the electrode potential. (English)

Breakdown Phenomena of Anodic Oxide Films on Titanium

K. Azumi and T. Ohtsuka

Zairyo to Kankyo, **46**, No.6, 384-390 (1997)

Voltammogram and impedance measurements were applied for analysing the change in electronic property of the anodic oxide film formed on titanium in neutral borate solution with the electrolytic breakdown at anodic potentials higher than the breakdown potential of 7.5 V. Anodic current histerisys was observed between the potential sweeps toward negative and positive directions for the film after the breakdown. The histerisys disappeared when the electrode was held at potentials lower than the breakdown potential. From analysis of the current histrisys it is suggested that high valency oxide such as TiO_3 or high valency state such as Ti^{5+} or Ti^{6+} are formed in the film at the breakdown. From the change of the Mott-Schottky plot with oxidation potential and period, it is estimated that the donor density in the oxide film increases after breakdown. (Japanese)

Pursuit of Electronic Property of the Passive Film on Titanium

K. Azumi, G. Yamamoto and M. Seo

Zairyo to Kankyo, **46**, No.3, 176-179 (1997)

To evaluate the corrosion resistance of passive film on titanium in reductive environment, change in electronic property of the anodic oxide film was pursuited with passage of time by using an impedance technique in neutral borate solution. When the passive film was formed at the potential noble than 6 V, the surface states was induced to the film which was eliminated at the potential less noble than 0.5 V. If the electrode potential was set at potentials less noble than -0.5 V, hydrogen penetration would occur to transform the film composition from TiO_2 to TiOOH with reducing electric resistivity of the film. If the potential was held between 0.0 V and -0.5 V, the gradual reduction of space charge layer thickness was observed. Although TiO_2 is considered to be stable from the view point of thermodynamics, the result suggests that the change such as hydration of the film may occur. (Japanese)

Impedance Study of Semiconductor Property of the Passive Film on Titanium

K. Azumi and T. Ohtsuka

Zairyo to Kankyo, **46**, No.3, 169-175 (1997)

The dielectric and semiconductive properties of the passive film on titanium were investigated under potentiostatic polarization in neutral phosphate and borate solutions by using the impedance technique. Further topographic change of the passivated surface with potential was observed by AFM. From comparison between the film thickness and the capacitance of the space charge layer, the dielectric constant of the passive film was estimated at about 40 in the potential region lower than 3 V and about 85 in the potential region higher than 3 V. From the Mott - Schottky plot the donor density of the passive film was calculated, which is in the order of 10^{26} m^{-3}, and decreased with an increase of the film formation potential. The decrease may correspond to a change of film structure from amorphous to crystalline. At potential higher than 7.5 V, breakdown of the passive film was observed, probably due to influence of very high electric field in the film. The breakdown brings about the increase of donor density, and a roughening surface due to micro-crystallization. (Japanese)

Trial for Evaluation of Heterogeneity of Passive Film on Iron by a Scanning Electrochemical Microscope.

Koji Fushimi and Masahiro Seo

Zairyo-to-Kankyo, **46**, No. 12, 797-803 (1997)

A scanning electrochemical microscope (SECM) was used to evaluate heterogeneity of passive films formed on iron in deaerated pH 8.4 borate solution. The probe current image and specimen current image for the specimen electrode, which consists of two iron plates embedded into epoxy resin, were measured with a tip-generation/substrate-collection (TG/SC) mode in deaerated pH 8.4 borate solution containing $[Fe(CN)_6]^{4-}$ as a mediator. The distinctions between epoxy resin and each iron plate were more clear in the probe current image than in the specimen current image. Moreover, the difference in thickness of passive film between two iron plates was distinguishable in the probe current image. The lateral resolution of the probe current image was about 40 μm which was two times as much as the diameter (20 μm) of the probe electrode. (Japanese)

The Metabolism of Sulfate-reducing Bacteria and Corrosion Behavior of Carbon Steel in the Continuous Culturing Medium

Fumio Baba, Tsuguo Suzuki and Masahiro Seo

Zairyo-to-Kankyo, **46**, No. 8, 498 - 504 (1997)

Carbon steel was exposed for long time to an inoculation continuous culturing medium of sulfate-reducing bacteria (SRB). The feed rate of medium was 10 cm^3 h^{-1}, and the concentration of Fe^{2+} of medium was kept to 0.01 mol kg^{-1}. The corrosion behavior and metabolism of sulfate-reducing bacteria (SRB) were investigated by measuring weight change of the specimens and by using a phase-difference microscope, hydrogen sulfide gas detector, and measuring the amount of ferrous sulfide in the medium. SRB evolved a significant amount of hydrogen sulfide and ferrous sulfide after the culture above 2 days. In the period of after the culture of 50 days, the medium contained 2 types of SRB with different shapes. One was rod like shape and the other was comma like shape. In this period, pH of medium was kept almost 7 without any pH adjusting. The weight of deposited film on the specimen increased linearly with culturing time, whereas the weight of the specimen substrate due to corrosion decreased linearly with culturing time. The corrosion rate in continuous culturing medium was 7 times as much as that in batch culture. (Japanese)

Effect of Different Types of Alkylaldehyde and Crystal Grain Size on the Morphology of a Localized Corrosion in Copper Tubes

Takenori Notoya

J. Mater. Sci. Letters,**16**,1406-1409(1997)

This paper clarifies the morphological features of the localized corrosion in copper tubes in the presence of six different types of aldehydes and in six different grain size copper tubes, in the presence of formic acid. The localized corrosion in copper tubes can be produced by a small amount of aldehydes. The severity of corrosion was in the increasing order of 1-heptanal, 1-dodecanal, propionaldehyde, acetoaldehyde, formaldehyde. No localized corrosion was observed in an atmosphere of benzaldehyde. The morphology of micro-pores, which developed in the micro-pits in the copper tubes was independent of the size of crystal grains. It is concluded that the localized corrosion is not a grain boundary attack. (English)

Localized Corrosion in Copper Tubes by Acetic Acid-Containing Seasonings

Takenori Notoya

Zairyo-to-Kankyo, **46**, 731-735 (1997)

One type of localized corrosion, known as ant's nest corrosion, in copper tubes is caused by decomposition products from chlorinated organic solvent and some types of lubricant oil. The decomposition products include carboxylic acids, acetates, formates and chlorides. Vinegar is mainly composed of acetic acid, which is one of the potential corrosive substances that cause this type of corrosion. 1-month and 3-months exposure tests were conducted in test tubes containing volatile acids, aldehydes and seven different vinegar-containing commercial seasonings. The severity and morphological features of this type of corrosion in copper tubes differed between types of corrosive substances and commercial vinegar-containing seasonings. The penetration depth and density of the localized corrosion in copper tubes exposed to commercial seasonings were not as great as those in copper tubes exposed to volatile acids and aldehydes.
(English)

Keynote Address: Localized "Ant's Nest" Corrosion in Copper Tubes Takenori Notoya

Proceedings of Corrosion & Prevention '97, paper 002, 1-8, (1997)

An unusual form of localized corrosion in copper tubes has been detected early in service and in leakage tests after manufacturing. The morphology of this corrosion is similar to that of an ant's nest when viewed in cross section. The sources of corrosives that promote the corrosion, influencing factors, corrosion mechanisms, cases of ant's nest corrosion, and preventive measures are presented. (English)

Inhibition Action of Benzotriazole Derivatives on Dissolution of Copper in Sulfuric Acid

Takenori Notoya

J. Japan Copper and Brass Research Association, **36**, 101-105(1997)

The inhibition action of six benzotriazole derivatives on copper dissolution in 2 M sulfuric acid at 25 C was compared with that of benzotriazole(BTA) by immersion tests and potentiodynamic polarization measurements. The inhibitors included BTA, 4-carboxy benzotriazole(4-CBT), 5-carboxy benzotriazole(5-CBT), 5-methyl benzotriazole(5-MBT), a mixture of 4- and 5-methyl benzotriazole(TTA), a mixture of 4- and 5-carboxy benzotriazole(CBT), and a newly-developed inhibitor, a mixture of 4- and 5-carboxy benzotriazole methyl ester(CBTME). The inhibitory action of BTA and its derivatives was shown to be mainly due to their adsorption on the copper surface from the results of surface enhanced Raman spectroscopy. The inhibition efficiency of the BTA derivatives, based on the results of immersion tests, was in the decreasing order of 5-CBT, CBTME, CBT, TTA, 4-CBT, 5-MBT, BTA. The 5-CBT gave the same inhibition efficiency as BTA at only one-tenth of 5-CBT's concentration. The 5-CBT and CBTME inhibited more an anodic dissolution process than cathodic processes, while TTa and CBT preferentially inhibited cathodic processes in copper corrosion. (Japanese)

Ant's Nest Corrosion in Copper Tubes: Questions and Answers

Takenori Notoya

Corrosion Engineering, **46**, 319-321(1997)

The characteristic features, causes, mechanisms and effective measures are described. Morphological characteristics of the ant's nest corrosion vary, depending on the corrosion medium, its concentration, temperature, oxygen level, and humidity. This type of corrosion has developed in an environment where water, oxygen, and volatile corrosive medium coexist. The final corrosion product of cuprous oxide is speculated to be formed by self-catalytic cyclic oxidation/reduction reactions of a water-soluble Cu-organic acid complex. Development of ant's nest corrosion for copper tube exterior surfaces can be inhibited by the removal of the residual corrosive medium and humidity control of the environment. (Japanese)

A Near-Infrared FT-Raman(SERS) and Electrochemical Study of the Synergistic Effect of 1-[(1',2'-dicarboxy)ethyl]-benzotriazole and KI on the Dissolution of Copper in Aerated Sulfuric Acid

D.P.Schweinsberg, S.E.Bottle, V.Otieno-Alego and T.Notoya

J.Applied Electrochemistry, **27**, 161-168(1997)

The adsorption on copper in aerated 0.5 M sulphuric acid of 1-[(1',2'-dicarboxy)ethyl]-benzotriazole(BTM) has been investigated by means of surface enhanced Raman scattering techniques. The inhibition efficiency in aerated acid increased with increasing BTM concentration to a maximum at the 1 mM level. Benzotriazole (BTAH) was found to be about 20% more efficient as an inhibitor for copper corrosion under the same conditions. BTM showed increased inhibition with increasing pH reaching a maximum value of 78.3% at pH 8. Polarization studies showed that BTM suppressed both the cathodic and anodic corrosion reactions. The SERS studies suggest that, like BTAH, BTM inhibits copper corrosion by adsorption through the azole nitrogen. This study also showed that the performance of BTM can be significantly improved by adding KI. SERS indicates that the iodide ions displace the protonated BTM on the copper surface and this is followed by an overlayer of protonated BTM molecules. (English)

Corrosion of Steel Fiber Reinforced Concrete

A.Keyvani Someh,N.Saeki and T.Notoya

Proc. Fourth CANMET/ACI International Conference on Durability of Concrete, Sydney, Australia, 451-466(1997)

Corrosion behavior and deterioration of galvanized steel fibers due to de-icing agents are discussed. The results of experiments concluded on fibrous concrete under a laboratory aggressive environments showed that steel fibers with a galvanized coating were very durable. Galvanized steel fibers showed a strong resistance to corrosion propagation caused by the use of de-icing salts. The volume expansion force of galvanized steel fibers due to corrosion products compared to that of common steel was negligible, and spalling phenomena of the concrete were not observed, even around the corroded fibers. (English)

Corrosion Protection Shield of Steel Bars, Due to Steel Fibers in Concrete

A.Keyvani Someh, N.Saeki and T.Notoya

Proc. Third CANMET/ACI International Conference, Auckland, New Zealand, 227-248(1997)

To generalize the galvanic protection behavior of steel fibers in the gel environment, the behavior of reinforced concrete specimens under an accelerated aggressive environment with both a no-fiber and fibrous concrete matrix were investigated. for this purpose, galvanized steel fibers were used. Corrosion phenomenon in the galvanized steel fibers contacting steel bars showed a sacrificial role of fibers in protecting the steel bars. No corrosion of the embedded steel bars occurred in the steel fiber-reinforced concrete matrix, while corroded steel bars occurred in the no-fiber reinforced concrete beam, thus confirming the merit of galvanized steel fibrous matrix as a protection shield to inhibit corrosion of reinforced concrete members. (English)

Application of a Vertically Stacked Bipolar Electrode Cell to Electrowinning of Liquid Magnesium from Chloride Melts

Tatsuo ISHIKAWA, Shoichi KONDA and Takeshi SASAKI

Denki Kagaku, **65**, 1080-1085(1997)

The design and construction of a vertically stacked bipolar electrode cell for electrowinning of liquid magnesium from chloride melts were described. Laboratory-scale electrolysis was carried out with the cell at 50 A for seven hours at about 750 ℃, and the cell construction was investigated in terms of the separation of magnesium particles from the flow of chlorine gas and the chloride melt circulating in the cell. The experimental results were discussed by using the net current efficiency which was concerned with the electrochemical reaction and/or chemical reaction. (English)

Consideration for Aluminum

T. Ishikawa

Denki Kagaku, **65**, 276-280(1997)

A view of the study on an electrowinning process of aluminum in chloride melts, which was proposed instead of the Hall-Heroult process, was presented. The process had a merit to save carbon materials without release of fluorine gas, and, moreover, to achieve electric power saving and high productivity, a new stacked bipolar electrode cell was developed modifying the cell proposed by ALCOA Co. Ltd. The method for analysis of electrolysis characteristics of the cell under operation was established. A novel electrochemical recovery process from scrap aluminum in chloride melts, one of whose steps was composed of a chlorine-cell for supplement of a part of electrolysis energy, was also proposed. (Japanese)

Electrorefining of Aluminum Containing Fe-, Mg- and Si-Components

Mikito UEDA, Shoichi KONDA, Takeshi SASAKI and Tatsuo ISHIKAWA

Proceedings of The 5th Internatinal Symposium on Molten Salt
Chemistry and Technology, 303-306(1997)

To develop a new process for electrorefining of Al from scrap aluminum by using a bipolar electrode system, electrolysis between aluminum-alloy anode and graphite cathode was carried out over 12 hours at 750 °C. Anodic behavior of 40 mass% Cu-Al alloys containing Fe-, Mg- and Si-components, and purities of aluminum recovered from the alloys were investigated. The results showed that Fe-contents in electrodeposited aluminum were under 0.01mass% and the Mg-components was negligible small; Mg dissolved into the melt, but no deposition occurred on the cathode. The Si-components were reduced to about 1/30 of anode alloys. The purity of over 99.9 mass% was achieved in recovering aluminum from tested alloys. (English)

Effect of a Small Amount of Hydrogen Chroride on High Temperature Oxidation of Nickel-Chromium Alloys

Yoshiyuki Sato, Motoi Hara, Yutaka Shinata and Toshio Narita

The Journal of Japan Inst. Metals, **61**, 56-63 (1997)

High temperature oxidation behavior of Ni-5, 10 and 20%Cr alloys in a 1%HCl-50%O_2-N_2 atmosphere was examined at 973-1273 K by thermogravimetry. Mass gains of the Ni-5 and 10%Cr alloys in the 1%HCl-50%O_2-N_2 atmosphere increased with time in the early stage of the reaction and then decreased to show negative values. On the other hand, mass gain of Ni-20%Cr alloy decreased with time from the early stage. Total metal consumption of these alloys showed a simple increase with time and with oxidation temperature. To investigate the mechanism of the reaction taken place at the stated conditions, the metal consumption were divided into two kinds of consumption, i.e. consumption for oxidation and chlorination. The metal consumption for oxidation increased with time in the earlier stage, and then showed a nearly constant value. In another hand, the metal consumption for chlorination appeared very small values at first, and then showed a constant rate at the later stage. Scales formed on the specimens had a layered construction. The inner scale around the metal/scale interface was porous. Scales formed on Ni-5 and 10%Cr alloys consisted of NiO, and an elemental Cr was detected in them. In the scales formed on Ni-20%Cr alloys, Cr_2O_3 Was identified. From all the results and a thermodynamic equilibrium discussion, it was revealed that oxidation and chlorination reactions took place simultaneously in the 1%HCl-50%O_2-N_2 atmosphere at high temperatures. It was also found that the addition of 20%Cr effectively reduced oxidation and chlorination in the HCl-bearing atmosphere. (Japanese)

Initial Oxidation of Type 430 Stainless Steels at 1073-1273 K.

Isao Saeki, Hidetaka Konno, Ryusaburo Furuichi, Tsuneo Nakamura, Katsumi Mabuchi, and Masahiko Itoh

J. Japan Inst. Metals, **61**, 417-424(1997)

Initial oxidation of type 430 stainless steels with 0.09 and 0.9 mass% Mn was studied at 1073-1273 K. For the steel with 0.09 mass% Mn, oxide growth took place ununiformly compared with the steel with 0.9 mass% Mn, resulting rougher surface with oxidation time. Concentration of Cr at the oxide surface on the steel with 0.09 mass% Mn, which is analyzed by X ray photoelectron spectroscopy, increased and Fe concentration decreased with the temperature, whereas for the steel with 0.9 mass% Mn, temperature dependence of surface concentration of Cr, Fe, and Mn was not simple. This complicated compositional change at the oxide surface was explained by a transformation phenomenon of the substrate metal. Oxide was composed of corundum type and spinel type oxides and the amount of the latter was found to relate to Mn and Cr content at the oxide surface. (Japanese)

Effect of Heating Rate on Properties of Initially Formed Oxides on Type 430 Stainless Steels at 1273 K.

Isao Saeki, Hidetaka Konno, Ryusaburo Furuichi, Tsuneo Nakamura, Katsumi Mabuchi, and Masahiko Itoh

Zairyo-to-Kankyo, **46**, 789-796(1997)

Type 430 stainless steels with 0.09 and 0.9 mass% Mn were heated to 1273 K with heating rates of 5, 33, and 50 K s^{-1}, and then oxidized in 0.165 atm O_2-balanced N_2 for up to 300 s, in which the total pressure was 1 atm and the flow rate of the gas was 200 cm^3 min^{-1}. The effect of the heating-up rate on the oxide thickness, morphology, and crystal structure has been studied. When the temperature reached to 1273 K with 50 K s^{-1}, an iron rich corundum type oxide with a thickness of 40 nm was formed for the steels with 0.09 and 0.9 mass% Mn. Contrary, the oxides with 5 and 33 K s^{-1} were composed of corundum type one rich in chromium and the thicknesses were two times thicker than that with 50 K s^{-1}. Spinel type oxide was also formed for the steel with 0.9 mass% Mn with 5 and 33 K s^{-1}. As the oxidation proceeds at 1273 K, the thicknesses of the oxides, surface composition, and crystalline structures became similar independent of the heating rates. The surface morphology and the amount of the spinel type oxide were, however, affected by the heating rate at relatively longer oxidation time. (Japanese)

High Temperature Oxidation of $MoSi_2$-WSi_2 Solid Solutions

Kazuya Kurokawa, Hiroki Matsuoka, and Hideaki Takahashi

Materials Science Forum, **251/254**, 885-892 (1997)

The effect of WSi_2 solute on the oxidation behavior of $MoSi_2$ was investigated in a wide temperature range of 773 K to 1773 K in air. $MoSi_2$ and WSi_2 individually have outstanding oxidation resistance at high temperatures such as 1773 K as a result of the selective oxidation of Si. Such passive oxidation behavior occurs also in all $MoSi_2$-WSi_2 solid solutions. On the other hand, at lower temperatures, especially at medium temperatures like 1073 K, accelerated oxidation which is based on the simultaneous oxidation of W and Si takes place for the 50% WSi_2 composition. In addition, it was experimentally confirmed that the preoxidation treatment at higher temperature is effective for prevention of the accelerated oxidation. (English)

Surface Patterning of Aluminum with Laser Irradiation and Electrochemistry

Hideaki Takahashi, Jun Wakabayashi, Kazutoshi Nukui, Masatoshi Sakairi,
Masahiro Seo, Yutaka Matsumi and Masahiro Kawasaki

Proc. 1st Intern. Symp. on Aluminium Surface Sci. and Tech., 344-349, (1997)

An attempt has been made to develop a new technology on the surface patterning of aluminum with laser irradiation and electrochemistry.

Aluminum specimens covered with anodic oxide films were immersed in solutions and were irradiated by a pulsed YAG laser through quartz window to remove the oxide film. After laser irradiation, localized anodizing or metal plating was attempted to form porous anodic oxide films or metal plating layer only at the laser-irradiated area. In localized anodizing, porous anodic oxide films were found to form at the selected area at a rate, which is lower than that obtained on the electropolished surface, and showed a pore-branching structure. Localized coloring was possible by dying with alizarine red. In localized metal plating, Cu- or Ni-layer was found to deposit on the laser-irradiated area by cathodic polarization in $CuSO_4$ or $NiSO_4$based plating solution. By changing the laser power, defocusing distance, and laser beam scanning rate with computer-controlled XYZ stages, micro patterns with Ni-plating layer were performed. (English)

Formation of Al/(Ti, Nb, Ta)-Composite Oxide Films on Aluminum by Pore-Filling

Masahiro Shikanai, Masatoshi Sakairi, Hideaki Takahashi, Masahiro Seo,
Katsumi Takahiro, Shinji Nagata, and Sadaei Yamaguchi

Journal of Electyrochemical Society, **144**, 2756 - 2766 (1997)

Aluminum specimens coated with porous anodic oxide films were dipped in solutions containing Ti^{4+}, Nb^{5+}, or Ta^{5+} ions, and heated in air mainly at 400 ℃, to deposit Ti-, Nb-, or Ta-oxide on the inner walls of pores. After 0 to 7 cycles of the dipping and heating process, the specimens were re-anodized in a neutral borate solution to fill the pores with Al_2O_3. The incorporation of Ti-, Nb-, or Ta-oxide in the anodic oxide films was examined by transmission electron microscopy, Rutherford back scattering spectroscopy, and impedance measurements.

Incorporation of Ti-, Nb-, or Ta-oxide was found only in the outermost part of the anodic oxide film after re-anodizing up to 400 V. The Al/Ti composite oxide films consisted of an outer Al/Ti-composite oxide layer, an intermediate crystalline alumina layer and an inner amorphous alumina layer, while the Al/Nb- and Al/Ta-composite oxide films consisted of an outer composite oxide layer and an inner amorphous alumina layer. The parallel electric capacitance of Al/Ti-composite oxide film was 40 % higher than the other two, due to its small thickness and high dielectric constant. The formation mechanisms of the composite oxide films during re-anodizing are discussed in terms of the ion transport across the oxide film. (English)

Formation and Breakdown of Anodic Oxide Films on Aluminum in Boric Acid / Borate Solutions

Yi Li, Hideki Shimada, Masatoshi Sakairi, Kazuhiro Shigyo,
Hideaki Takahashi and Masahiro Seo

J. Electrochem. Soc., **144**, 866-876 (1997)

Highly pure aluminum was anodized at a constant current density of 25 A m^{-2} at 293 K in 0.5 M boric acid / (0, 0.005 or 0.05) M sodium tetraborate solutions, to examine the effect of sodium tetraborate concentration on the formation and breakdown characteristics of barrier oxide films, by using inductively coupled plasma atomic emission spectrometry (ICP-AES), electroluminescence (EL) / photoluminescence (PL) measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical impedance spectroscopy (EIS).

In boric acid/borate solutions, a crystalline alumina formed locally in the middle of the amorphous oxide film. Above the crystalline alumina, a void is formed and may lead to a breakdown of the oxide film at 420 ~ 540 V.

In boric acid solution, an amorphous oxide film grew until 1180 V with the formation and development of imperfections, and with enhancement of electroluminescence and gas evolution. At imperfections, the oxide / solution interface was convex and oxide / metal interface curved in the opposite direction. This deformation is attributed to high pressure O_2 evolved in the pores of imperfections and to local formation and dissolution of oxide. The breakdown of the oxide film started when the O_2 evolution and oxide dissolution at imperfections become predominant.

The mechanism of formation and breakdown of the anodic film in the boric acid / borate solutions is discussed in terms of pH-buffering of the anodizing solution, and the electronic structure of anodic oxide films is correlated with EL and PL spectrum results. (English)

Nanostructure, Composition and Luminescence Properties of Porous Silicon Layer Subjected to Various Surface Treatments

K. Shigyo, K. Azumi and M. Seo

J. Surface Analysis, **3**, No.2, 502-510 (1997)

A porous silicon layer (PSL) was prepared on p-type silicon (100) wafer with electrochemical etching in HF aqueous solution. The PSL was subjected to the surface treatments (anodic oxidation, dip into HF aqueous solution, dry oxidation, hydrothermal oxidation) to examine the correlation between nanostructure, crystallinity, composition and visible luminescence properties of PSL. The nanostructure and crystallinity of PSL were investigated by TEM observation and the surface characterization were performed by using FT-IR and XPS. The spectra of photoluminescence (PL) were measured to examine the visible luminescence properties. The high resoultion TEM images and TED patterns showed that the PSL as prepared with electrochemical etching consists of Si particles with a diameter of 2 nm - 3 nm and has a mosaic structure of crystal and amorphous. The PSL subjected to anodic oxidation or hydrothermal oxidation has an amorphous structure. It is found that the visible PL intensity increases with decreasing concentration of silicon hydrides (SiHx) only for the PSL prepared under different electrochemical etching conditions. The PL intensity of PSL was enhanced significantly by HF dip treatment after anodic oxidation or by hydrothermal oxidation. No correlation between nanostructure, crystallinity, composition (SiHx, elemental Si and SiO_2) and PL intensity was observed for the PSL subjected to the surface treatments. The reason for no correlation was explained in terms of the difference in information depth between FT-IR, XPS and PL emission or in depth-distribution between each constituent (SiHx, elemental Si and SiO_2) and PL center. (English)

Effects of Ceramic Strength and Ni-Interlayer Thickness on Fracture Strength of Si_3N_4 Ceramic/Stainless Steel Joint

Shouhei Hata and Toshio Narita

The Journal of Japan Inst. Metals, **61**, 1255-1259 (1997)

Fracture strength of Si_3N_4 ceramics joined to stainless steels with a Ag-Cu-Ti filler and a Ni(0.02～0.5mm)/W/Ni interlayer was investigated as functions of the ceramic strength and Ni-interlayer thickness.

For the joints with a 1500 MPa ceramics fracture strength of the joints increased monotonously with decrease of Ni-interlayer thickness from 300 MPa at 0.5 mm to 660 MPa at 0.02 mm For the joints with 800 and 1100 MPa ceramics, however, the fracture strength decreased rapidly when the Ni-interlayer was thinner than 0.25mm. This degradation seems to be due to cracks formed during a bonding process. The effect of ceramic strength on the fracture strength of ceramic/'metal joints was hardly observed when these pre-cracks were eliminated from the joints.

It is suggested that the bonding layer plays decisive role in the fracture strength of ceramic/metal joints in addition to the thermal residual stress, irrespective of the ceramic strength itself. (Japanese)

Metallizing of Silicon Carbide Ceramics with Titanium Vapor

Toshiyuki Takashima, Masahiro Washida,
Tsuyoshi Yamamoto and Toshio Narita

Journal of the Ceramic Society of Japan, **105**, 68-72(1997)

Silicon-carbide ceramic was metallized with titanium by the vapor-diffusion method, where pure titanium powder was used as a vapor source at temperatures between 973 and 1323 K for up to 296.1 ks in a dynamic vacuum atmosphere. The structure and composition of the metallized layers were investigated by scanning electron microscopy, electron-probe microanalysis, and X-ray diffraction analysis. At the initial stage of the metallization, titanium vapor reacted preferentially with the so called free carbon in the grain boundaries of SiC ceramics to form a titanium carbide, and then a metallized layer was grown laterally, forming the sub-layer structures. This sub-layer structure was composed of five sub-layers; TiC (top surface) , Ti_5Si_3 containing TiC (outer layer), TiC containing Ti_5Si_3 (middle layer) , Ti_5Si_3 (inner layer) and Ti_3SiC_2 (bottom layer) . Growth kinetics of each sub-layer and their total thicknesses obeyed the parabolic rate law, and the parabolic rate constants (kp) for the total layer varied between 10^{-16} $m^2 \cdot s^{-1}$ at 1173 K and 10^{-15} m^2. s-1 at 1323 K. The activation energy (Qkp) obtained for the metallized layer was 153 $kJ.mol^{-1}$. (Japanese)

Structures and Formation Behaivior of Coating Layer in Two-step Zn-Al Hot-Dipped Steel

Junichi Tanaka, Yusaku Masuda, Tomoaki Takechi,
Mitugu Sakaguchi and Toshio Narita

The Journal of the Surface Finishing Society
of Japan, **48**, 929 - 936(1997)

Structures and its formation behavior of coating layer formed on steel by two-step hot-dipping method i.e., primary dipping in a zinc bath followed by immersion in a secondary Zn-7mass%Al bath , were studied using scanning electron microscope (SEM), electron probe micro-analysis (EPMA) and X-ray diffraction analysis (XRD). Primary dipping layers composed mainly of ζ phase and trace of η phase. The columnar structure changed to a fine acicular structure with a Fe_4Al_{13}-ZnX phase at temperatures below 693K. Above 703K, it became a two-phase structure of a plate-like Fe_2Al_5-ZnX and a fine broken acicular Fe_4Al_{13}-ZnX phase. A Zn-Al coating layer over 50μm thick was obtained by secondary immersion between 683K and 733K for steel dipped into a primary bath at 763K. (Japanese)

Reaction between Fe-Zn Alloy Layer and Zn-AL Melt

Junichi Tanaka, Yusaku Masuda, Ryouji Masumoto
Kenichi Ohsasa and Toshio Narita

The Journal of the Surface Finishing Society
of Japan, **48**, 1012 - 1018(1997)

Reactions between Fe-Zn alloy layer coatings formed on the Fe specimen surface hot-dipped in Zn melt (primary melt) and Zn-Al melt (secondary melt) were investigated. In order to determine the formation mechanism of alloy layer coatings, as dipped coatings containing Zn melt and annealed coatings without Zn melt were dipped into secondary melt, and their microstructures and solute concentration distributions in coatings were compared. Coatings containing Zn melt and Zn-Al melt reacted rapidly because the reactions controlled by rapid Al and Zn diffusion in Zn melt. Annealed coatings and Zn-Al melt reacted relatively slow because the reaction is controlled by solid diffusion in Fe-Zn alloys in coatings. (Japanese)

Surface Pretreatment Effects on Zn Deposition in Zincate Process of Aluminum Alloy

K. Azumi, Y. Fujishige, M. Seo, I. Saeki, L. Nanis, H. Nakao and K. Tashiro

J. Surface Finishing Soc., Jpn., **48**, No.10,1019-1024 (1997)

Surface pretreatment effects of Al and Al-Mg alloy on Zn deposition in the zincate process were evaluated using SEM and XPS. Al surface dissolution in a concentrated NaOH solution followed by zincate treatment produced rapid Zn particles nucleation with uniform size due to Al surface oxide film thinning. The anodic oxidation pretreatment of Al used jointly with electropolishing followed by zincate treatment also resulted in deposition of uniform Zn particles. Anodic oxidation pretreatment without electropolishing, however, resulted in nonuniform Zn deposition indicating that defects in the oxide film could be active sites for Zn nucleation. Al-Mg alloys require both alkaline and acid cleaning in surface pretreatment because Al dissolves in concentrated alkaline solution, and Mg dissolves in acid solution. Magnesium or its enriched compounds on the surface during zincate process in an alkaline zincate solution inhibits Al dissolution and Zn deposition. XPS showed that Zn^{2+} remains in the Al oxide layer, which partially charged after Zn stripping in a HNO_3 solution. The role of the first zincate process in double zincate treatment is discussed based on these results. (Japanese)

Effect of dry density on activation energy for diffusion of strontium in compacted sodium montmorillonite

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

Scientific Basis for Nuclear Waste Management XX, 893-900 (1997)

For performance assessments of geological disposal of high-level radioactive waste, activation energies for the diffusion of strontium ions and the basal spacing of compacted sodium montmorillonite in the water-saturated state were determined.

Basal spacing determined by XRD indicated changes in the interlamellar space from a three-water layer hydrate state to a two-water layer hydrate state as the dry density of the montmorillonite increased from 1.0 to 1.8 Mg m^{-3}. Activation energies from 17.3 to 30.8 kJ mol^{-1} for the apparent diffusion coefficients of strontium ions were obtained. The lower activation energies than for diffusion of strontium ions in free water were determined for montmorillonite specimens of lower dry density (1.2 Mg m^{-3} and below), while the higher activation energies were at higher dry densities (1.4 Mg m^{-3} and above).

These findings cannot be explained by changes in only the geometric parameters, which the pore water diffusion model is based upon. Possible explanations for the dry density dependence of the activation energy are the changes of the temperature dependence of the distribution coefficients and/or of the diffusion process with increasing dry density.

Radioactive Waste Management-Development of Technologies and Projects in Japan

Takehiko Ishihara and Hiroshi Ohashi, Editors and Authors
Japan Atomic Industrial Forum, Inc., in July 1997

The contents included in a 404 pages volume are as follows;

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Part 2 High level radioactive waste management
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(Japanese)

Effects of humic acid on the sorption of neptunium (V) on kaolinite

Yoshinobu Niitsu, Seichi Sato, Hiroshi Ohashi, Yoshiaki Sakamoto,
Seiya Nagao, Toshihiko Ohnuki, Susumu Muraoka

Journal of Nuclear Materials, **248**, 328-332 (1997)

The sorption coefficient of Np (V), Kd, on kaolinite was measured at pH 6 to 11 and in humic acid concentrations of 0 to 40 mg dm^{-3} at the ionic strength of 0.1 M. The Kd value increased with pH both with and without humic acid. The Kd value increased slightly with increasing concentration of humic acid in the pH range below 8 and decreased not more than an order of magnitude with increasing concentrations of humic acid in the pH region above 8. Below pH 8, Np (V) sorption is considered to be enhanced by the sorption of humic acid on the kaolinite to form Np (V)-humate complexes. Above pH 8, it is probable that the desorption of humic acid and formation of Np (V)-humate in solution result in the decrease of Kd. The behavior of Np (V) sorption on kaolinite with humic acid is described by a simple model. (English)

Migration behavior of palladium in uranium dioxide

Mitsuru Yoneyama, Seichi Sato, Hiroshi Ohashi, Toru Ogawa,
Akinori Ito, Kousaku Fukuda

Journal of Nuclear Materials, **247**, 50-58 (1997)

The migration behavior of palladium in UO_2 was investigated by determining the concentration profiles of Pd in UO_2 at temperatures from 1573 to 2073 K in Ar + 3% H_2. Pd was found exclusively in the pores of UO_2. The maximum penetration depth of Pd was more than 100 μm for the pellet of 90% TD and about 50μm for the pellet of 95% TD for 100h at 1623 K. Melted Pd wetted UO_2 well and U was detected both in precipitates and in Pd sources, forming an α-Pd phase containing U at about 10 at%. On the basis of thermodynamic calculations, it was found that a UPd_3 and Pd alloy containing U can form even under the oxygen potential, where O/U ratios were slightly higher than 2.00, say 2.000-2.003. From the above results, a model of the gaseous diffusion of Pd through pores in UO_2 retarded by the formation of U-Pd alloy was proposed. (English)

Thermal expansion and thermal conductivity of cesium molybdate

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

Journal of Alloys and Compounds, **255**, 18-23 (1997)

The temperature dependence of the lattice parameters of Cs_2MoO_4 was measured using the high-temperature X-ray diffraction method, 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 773K, which was more than four times that of UO_2. The thermal diffusivity of Cs_2MoO_4 was measured by the laser flash method from room temperature to 1000K. The thermal conductivity of Cs_2MoO_4 was evaluated from the measured thermal diffusivity and bulk density, and the specific heat capacity available in the literature. 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 1000K. (English)

Anomalous Gamma Peak evolution from SrCe Solid State Electrolyte Charged in D_2 Gas

Tadahiko Mizuno, Koich Inoda, Tadashi Akimoto, Kazuhisa Azumi, Masatoshi Kitaichi, Kazuya Kurokawa, Tadayoshi Ohmori and Michio Enyo

International Journal of Hydrogen Energy, **22**, 23-25 (1997)

A proton conductor, the solid state electrolyte, made from oxide of strontium; cerium, niobium and yttrium can be charged in a hot D_2 gas atmosphere. Anomalous radioisotopes were detected for samples charged by alternating current for 5 to 45 Volts at temperatures ranging from 400 to 700 degree. None kinds of radioisotopes were detected from the sample treated in H_2 gas atmosphere. This radioisotope may be induced from a catalytic reaction between metal and oxide interface to deuterium atoms. Samples were made from a mixture of metal oxide of Sr, Ce, Y and Nb. These powdered oxides were first mixed, and then sintered in an electric furnace at 1400 ℃ in air for 16 hours. The samples were pulverized, and mixed, alcohol was added, and the samples were put in a pressing machine and formed into round plates of 20 mm in diameter and 1 mm thick. These plates were again sintered at 1300-1480 ℃ in air for 16 hours. Sample densities were ranged from 3.0 to 5.2; the theoretical density for perfectly sintered sample is 5.8. Both sides of the sintered sample were then coated with porous Pt film, by painting a Pt organic compound and deposition in 700℃ or coated by Ar sputtered to Pt in vacuum. The resulting Pt film thickness was 0.15-0.3 μm. The film is porous and very rough surface; Hydrogen gas easily passes through the film and reaches to ceramic surface. Schematic representation for measurement system and reacting system are shown in figure 1 and 2 respectively. Experimental procedures are described as follows: (1) the reactor cylinder is evacuated by a rotary and diffusion pump (with liq. N_2 trap) to 2×10^{-5} Torr. (2) Sample temperature is raised to 400～700 ℃. (3) Gas is introduced into the cylinder at 0.1～50 Torr. (4) The sample is charged with EPD power at 5～45 Volts alternating power, with frequency set between 10^{-4} and 1 Hz depending on the sample temperature and thickness. (5) All the samples were tested for the gamma ray detection by Ge (Li) detector before and after the electrolysis. (English)

Transmutation in the Electrolysis of Light Water-Excess Energy and Iron Production in a Gold Electrode

Tadayoshi Ohmori, Michio Enyo, Tadahiko Mizuno, Yoshinobu Nodasaka and
Hideki Minagawa,

Fusion Technology, **31**, 210-218 (1997)

We have confirmed using several analytical methods that many kinds of new elements are produced on/in Au electrode after the electrolysis in light water solutions. The products were Fe, Zn, Cr, Cu, Ca, Ti and Si and Mg as the products were detected only by the electrolysis at an extremely high current density. The mass spectrometry analysis was carried out for many kinds of elements over mass numbers of 1 to 208. The isotopic compositions of above elements were significantly different from these natural isotopic distributions. For example, the isotopic composition of natural iron is 5.8% Fe54, 91.72% Fe56, 2.2% Fe57 and 0.28% Fe58. On the other hand, in the case of iron produced on/in an Au electrode content was 5% Fe54, 62% Fe56 and 33% Fe57. It is known that the natural isotopic distribution varies only by less than 0.003% for iron. Essentially the same phenomenon was confirmed more than ten times under the electrolysis condition at a current density of 0.2 A/cm^2. All the possibilities of the influence of contamination on the experimental precision had been carefully eliminated by keeping the electrolysis system in a very purified condition. We concluded from above results that some transmutation reactions take place during the electrolysis and above elements with anomalous isotopic distribution are the products of the nuclear transmutation reaction. This suggests that some new interaction work among protons, electrons and electrode material atoms, which becomes the origin of the new phenomenologies observed in this study. (English)

Low Temperature Nuclear Transmutation forming Iron on/in Gold Electrode during Light Water Electrolysis

Tadayoshi Ohmori, Tadahiko Mizuno, Hideki Minagawa and Michio Enyo

Int. J. Hydrogen Energy, **22**, No.5, 459-463 (1997)

Quantitative analysis and isotopic Quantification of Fe atoms which appeared to be produced during the electrolysis with Au electrodes in Na_2SO_4 light water solutions were studied. The electrolysis was performed for 7 days with a current of 1 Ampere. After the electrolysis the elements on/in an electrode were analyzed by means of AES. In every case a notable amount of Fe atoms, in the range of 1016-1017 atoms/cm^2, were detected together with the evolution of a definite amount of excess heat. The isotopic abundance of the Fe atoms were measured by means of SIMS, which were 6.5, 77.5 and 14.5 % for Fe54, Fe56 and Fe57 respectively, at the top surface of the Au electrode, which were obviously different from the natural ones. (English)

The Co^{2+} Adsorption Properties of Al_2O_3, Fe_2O_3, Fe_3O_4, TiO_2 and MnO_2 Evaluated by Modeling with the Frumkin Isotherm

Hiroki Tamura, Noriaki Katayama, and Ryusaburo Furuichi

J. Colloid Interface Sci., **195**, 192-202 (1997)

Adsorption of Co(II) ions on metal oxides is related to radioactive ^{60}Co(II) (de)contamination of nuclear power plants, Co(II) ion retention in soils as plant nutrition, concentration of Co(II) in deep-sea manganese nodules, and other applications. Here, the amount of adsorbed Co(II) on metal oxides was measured as a function of the pH and concentration of Co(II) ions, and the adsorption properties of metal oxides were evaluated with a model that considers simultaneous (1:1) and (1:2) exchange reactions between Co^{2+} aqua ions and surface hydroxyl protons obeying the Frumkin isotherm. The possibility of participation of mono- and polynuclear Co(II) hydroxo complexes in the adsorption was examined, and it was suggested that these species play no role under the conditions here. From the model parameters, it was found that the Co^{2+} adsorption ability of metal oxides increases in the order: $Al_2O_3 < Fe_2O_3 < TiO_2 < Fe_3O_4 < MnO_2$, showing a good correlation to the electronegativity X_i of the lattice metal ions of the oxides. The Co^{2+} adsorption was divided into two processes: 1) deprotonation of surface hydroxyl sites and 2) bonding of Co^{2+} to the deprotonated sites with a negative charge. With increasing X_i, process 1) increases possibly due to the decrease in the donor electron density responsible for covalent bonds with protons, while process 2) changes only slightly. It was suggested that process 2) is due to ionic bond formation ("electrostatic contact adsorption"), which is independent of the donor electron density, and the correlation of the overall process to X_i found here was ascribed to process 1) above. (English)

Adsorption Affinity of Divalent Heavy Metal Ions for Metal Oxides Evaluated by Modeling with the Frumkin Isotherm

Hiroki Tamura and Ryusaburo Furuichi

J. Colloid Interface Sci., **195**, 241-249 (1997)

Adsorption of divalent heavy metal ions, M(II), on metal oxides is important to determine the behavior of ions in waters and soils. The amount of adsorbed Pb(II), Cu(II), Zn(II), Co(II), Ni(II), and Mn(II) ions on the two oxides MnO_2 and Fe_2O_3 was measured as a function of the pH and concentration of the ions under the conditions where no mono- and polynuclear hydroxo complexes play a role in the adsorption. The adsorption affinity of these ions for the oxides was evaluated with a model that considers simultaneous (1:1) and (1:2) exchange reactions between M^{2+} aqua ions and surface hydroxyl protons (surface complexation) obeying the Frumkin isotherm. From the model parameters, it was found that the affinity order for (1:1) complex formation is $Cu^{2+} > Mn^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$ for MnO_2 and $Pb^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+}$ for Fe_2O_3. A large affinity of Mn^{2+} for MnO_2 was ascribed to the oxidation of this ion by MnO_2. A good correlation between the stability constants of (1:1) surface complexes and those of (1:1) hydroxo complexes in solution was obtained. The adsorption affinities of ions here are the affinities for deprotonated hydroxyl sites with negative charge, since for all the ions the oxides are common and the deprotonation properties of hydroxyl sites are the same. The good correlation suggests that the two reactions are similar: From electrostatic theory including crystal field corrections, the both reactions could be regarded as due to ionic bond formation between the positive charge of metal ions and the negative charge of deprotonated sites on oxides or hydroxide ions in solution, as we have suggested previously. (English)

In-Situ Synthesis of Fully Dense $MoSi_2$-SiC Composites by Spark Plasma Sintering

Kazuya Kurokawa, Makoto Ube and Hideaki Takahashi

Proc. 1st Inter'l Sympo. on Applied Plasma Sci., 129-134 (1997)

Spark plasma sintering (SPS) has been used to prepare fully dense MoSi2-SiC composites. In the sintering, elemental Mo, Si and C powders were used for in-situ synthesis. The results of diffrencial thermal analysis and X-ray diffraction patterns showed that both of $MoSi_2$ and SiC were formed at about 1700 K and the reaction of Mo with Si to form $MoSi_2$ had a high calorific value. Densification of the mixed powders proceeded rapidly by the formation of $MoSi_2$. However, the most suitable temperature for sintering of the mixed powders depended on the content of SiC. Higher temperatures was required for sintering of formed SiC. Fully dense $MoSi_2$ and $MoSi_2$-SiC composites can be prepared by spark plasma sintering of Mo, Si and C powders. (English)

Simulation of Grain Structures in High-manganese Steel Casting

Hitoshi Ishida, Koichi Sakamoto, Syogo Murakami,
Tatsuhiko Kusamichi and Kenichi Ohsasa

R&D Kobe Steel Engineering Reports, **47**, 58-61(1997)

A new algorithm based upon the Monte Carlo technique, previously used to develop a computer simulation of micro recrystallization and solidification was proposed for the simulation of grain structure solidification. This method was applied to high-manganese steel casting to predict the condition of grain refinement. The grain structures from the simulation were in good agreement with that of the high-manganese steel ingots. Furthermore, the transition temperature from columnar to equiaxed structures was successfully predicted by this simulation technique. (Japanese)

Fabrication and Properties of Functionally Graded Dental Implant

F. Watari, A. Yokoyama,, F. Saso, M. Uo & T. Kawasaki

Composites Part B, **28B**, 5-11 (1997)

Dental implants with functionally graded structures composed of titanium(Ti) and ceramic hydroxyapatite(HAP) were fabricated to satisfy both mechanical and biocompatible property requirements. Specimens containing up to Ti/50%HAP functionally graded material(FGM) with the dimensions 6x15mm were successfully fabricated by CIP and sintering process. Miniature (2x10mm) specimens of Ti, Ti/20%HAP FGM and Ti/30%HAP FGM implants were then made and inserted into femora of ten week-old Wistar strain rats to evaluate their biocompatibility. After 1,2 and 4 weeks of implantation, the rats were sacrificed and tissue blocks containing the implant material were embedded in resin. Observation of bone formation around the implant was performed by both the conventional method by optical microscopy using specimens stained with toluidine blue and the EPMA mapping method using unstained specimens. The observed area of new bone formation was in good agreement for both the light microscopy and EPMA elemental mapping method. Pure Ti and Ti/HAP FGM specimens showed no inflammation. When pure Ti and Ti/HAP FGM specimens were compared, Ti/HAP FGM showed better biocompatibility. (English)

Elemental mapping of functionally graded dental implant in biocompatibility test

F. Watari, A. Yokoyama, F. Saso, M. Uo, S. Ohkawa & T. Kawasaki

Proc. 4th Int. Symp. on Functionally Graded Materials, 749-754 (1997)

The dental implant must have both mechanical strength and biocompatibilty as its functuion. The HAP implant made of hydroxyapatite(HAP) has the very good compatibility with the bone. However it is brittle and often broken down by the mechnical shock. In the case of the metal implant coated with HAP film by plasma splay, the film was sometimes peeled off or absorbed in the tissue. Functionally gradient structure would be the useful conception to be applied for such a case in the biomaterials. The implant was made with the graded structure in the longitudinal direction from pure Ti in the top, increasing the HAP content, toward the bottom which is supposed to be implanted inside the jaw bone. To evaluate the biocompatibility the miniature(2x10mm) functionally graded implants were inserted in the femora of rats and also inside the jaw bone of rabbits for 1 to 4 weeks. The bone formation was observed by reflection electrons for the unstained and non-coated cross-section of the specimen. The reflection electron image was compared with the usual secondary electron image in SEM. The bone formation was then observed for each bone forming element by EPMA mapping for the unstained specimen. These results were compared with the histological observation by conventional method using the optical microscopy for the thin transparent stained specimen.

The usual secondary electron image in SEM showed the typical electron charging effect causing the very noisy image which made it impossible to obtain the proper information. The reflection electron image using the semi-conductor detector provided us the clear image without noise. The difference of reflectivity of electrons by atomic number effect gave Ti matrix the brightest contrast and the contained HAP particles enough brightness. The newly formed bone which is rich in Ca was clearly recognized surrounding the implant in the dark contrast region which is mainly composed of the protain. The EPMA elemental mapping showed the further information. The Ca and P mapping images showed the distribution of HAP particles inside the Ti matrix and the newly formed bone surrounding the implant. The new bone was formed apart from the implant material in 2 week implantation and grown in direct contact to the surface of the material in most area after 4 weeks. The implant showed the sufficient biocompatibility. (English)

Development of dental implant with functionally graded structure

F. Watari, A. Yokoyama, F. Saso, M. Uo, H. Matsuno & T. Kawasaki

FGM News, **34**, 13-17 (1997)

The dental implant composed of biocompatible metal, Ti, and ceramics, hydroxyapatite(HAP), with the structure of functionally graded materials(FGM) was fabricated in the size 6 ϕ x15mm by CIP and sintering process to satisfy both mechanical properties and biocompatibility. The gradual change of concentration in the longitudinal direction of implant was confirmed by the analysis of elemental distribution using EPMA. Animal implantation test was done using the miniature(2 ϕ x10mm) specimens of Ti, Ti/20%HAP FGM and Ti/30%HAP FGM implants to evaluate biocompatibility. The new bone formation around the implant was clearly observed by EPMA elemental mapping method using the unstained specimen. Ti/HAP FGM specimens showed no inflammation and a direct contact of newly formed bone on implant surface after 4 week, suggesting a sufficiently good biocompatibility. (Japanese)

The Chemical and Biochemical Functionally Graded Materials
-Fabrication of Functionally Graded Dental Implants-

F. Watari, A. Yokoyama, F. Saso, M. Uo & T. Kawasaki

Report of Grant-in-Aid for Scientific Research on Priority Areas,
No.274, 373-378 (1997)

The dental implant composed of biocompatible metal, Ti, and ceramics, hydroxyapatite(HAP), with the structure of functionally graded materials(FGM) has been fabricated to satisfy both mechanical properties and biocompatibility. The FGM implant with the graded structure increasing the HAP content from pure Ti at one end to the other in the longitudinal direction was made through the process of packing, compacting by CIP and sintering at 1300℃ in vacuum. The miniature FGM implant of the cylindrical shape 2x7mm was possible to fabricate up to Ti/20HAP by applying the CIP pressure 400MPa and Ti/100HAP by applying 1000MPa. After the implant was inserted in the mandible of rabbits for 1-8 weeks, elemental mapping and other imaging methods by Electron probe microanalysis(EPMA) and X ray scanning analytical microscopy(XSAM) as well as optical microscopy were applied for the evaluation of new bone formation around the implant. The growth of new bone formation around the part of Ti-20HAP of FGM implant is shown with the images of Ca elemental mapping obtained by XSAM after 1, 4, 8 week implantation. The implant located in the center is mainly composed of Ti and not visible. The new bone is formed only partially around the implant and not contact to the implant after 1 week. After 4 week the new bone is surrounding nearly the whole circumference of the implant. After 8 weeks the implant is completely surrounded by new bone, which is more dense and matured.The mapping method used in this study is simple and easy to evaluate the growth of new bone formation. The ultra thin section with staining treatment is necessary in the conventional method using an optical microscope, wheras the mapping method needs no staining, because the contrast arises from the intrinsic properties of specimen and it is a non-transparent method which allows the thick specimen applicable. No inflammation was observed throughout the implants fabricated and inserted in the mandible of rabbits according to the animal experiments. The Ti/HAP FGM implants showed enough good biocompatibility. (Japanese)

Study on fabrication and biocompatibility of Ti/HAP functionally graded materials

F. Saso, A. Yokoyama, F. Watari & T. Kawasaki

Hokkaido J. Dental Science, **18**, 85-104 (1997)

Functionally graded materials(FGM), a recent development in composite materials, consist of a continuously graded zone instead of a discrete interface between two component phase. The concept of FGM as applied for biomaterials in this study.In order to satisfy the requirements of both mechanical and biocompatible properties, dental implants with FGM structures composed of metal titanium(Ti) and ceramic hydroxyapataite (HAP) were fabricated and their properties were investigated. The powders of Ti and HAP with different mixed ratio were packed into the mold to make the gradience of concentration .The mold was than compressed by CIP .The compact of powders was sintered at 1300℃, 2hr in10-5torr. FGM specimens with the dimensions 2x10mm containing up to 20%HAP (Ti/20%HAP) were fabricated by CIP pressure of 400MPa. FGM specimens from pure Ti to 100%HAP could be made by the improvement of mold and the increase of CIP pressure up to 1000Mpa. Thermally contractive vynyl pipe with very small thickness(0.25mm) was adopted for mold. The structure of FGM specimens was confirmed from external appearance and cross-section.These specimens were also investigated by SEM and EPMA(electron probe microanalyzer). The mapping of Ti, Ca, P elements showed clearly the gradient concentrate of Ti and HAP. The Brinell hardness was 71 and 63 in 100%Ti area and 100%HAP area. The hardness of the area in better was lower. These specimens were implanted in mandibles of thirteen week-old Newzealand white rabbits to evaluate their biocompatibillity. After 4 and 8 weeks of implantation, these rabbits were sacrificed and tissue blocks containing the specimens were embedded in resin. Observation of biocompatibillity was performed by both the conventional method by optical microscopy using specimens stained with villanueva bone stain liquid and the EPMA mapping method using unstained specimens. The observed area of newly formed bone was in good agreement for both the optical microscopy and EPMA mapping method. Pure titanium and Ti/20%HAP FGM specimens showed no inflammation. When two specimens were compared, FGM showed slightly better biocompatibility. When 100%Ti area and 20%HAP area in a FGM were compared, there was very litle difference in the new bone formation. The results suggest that FGM implants was satisfied with the requirements of both mechanical and biocompatible properties. (Japanese)

Mechanical Properties and Estheticity of New FRP Orthodontic Wire

T. Imai, M. Kobayashi, F. Watari, S. Yamagata, K. Nagayama and S. Nakamura

J. Dent. Res. **76**(IADR Abstracts), 401, 1997.

Esthetic orthodontic wires of transparent fiber reinforced plastic(FRP) structure were newly fabricated and mechanical properties were investigated. Multiple fibers of biocompatible CPSA glass and PMMA matrix were formed into FRP wire of 0.5mm in diameter by drawing at 250℃. Long glass fibers of 8-20μm in diameter were unidimensionally oriented to the longitudinal direction. Fiber fraction was changed from 28% to 60%. The 3 point flexural test was done up to the deflection 2mm for the 14 mm span. The test was also done in water changing temperature between 25 and 50℃. Stress-strain curves of FRP wire showed a very good elastic recovery after deformation similar to superelastic Ni-Ti. Young's modulus E and the flexural load at deflection 1 mm P showed very little dependence on glass fiber diameter and linear dependence on fiber fraction V, complying with the rule of mixture for composites. This dependency was expressed as E(GPa)=2.21+0.698V(%) for Young's modulus and P(MPa)=0.36+0.039V(%) for flexural load. By changing fiber fraction from 28 to 60%, the load could be changed from 1.3 to 2.7N, which could cover the most range of strength corresponding to metal wires from Ni-Ti to Co-Cr. The change of lord by the change of temperature was smaller than Ni-Ti wire. FRP wire was transparent and had enough estheticity. Thus FRP wire composed of multiple glass fibers and PMMA matrix could satisfy both mechanical properties necessary for orthodontic wire and an esthetic effect. (English)

New Fabrication Method of Porcelain Inlay Using Cold Isostatic Press

C. Kawamoto, F. Watari & H. Shimokobe

The Japanese J. Conservative Dentistry, **40**, 1408-1426 (1997)

Porcelain has long been prized as an excellent aesthetic restorative material offering both biocompatibility and chemical stability. Its advantages have been reconfirmed recent years with the improvement of adhesion technologies. Production of porcelain inlays is, however, still complicated and requires special skills. Adaptability to cavities and mechanical properties vary depending on the skill of each operator. The conventional method also has problems such as deterioration of strength and formation of micro-crack due to the multiple firings of the material. In this study, therefore, the cold isostatic press (CIP) method, which is generally applicated for the industrial powder molding of ceramics, was adopted to simplify molding and homogenize products, and a porcelain inlay production process using CIP was examined. Furthermore, the mechanical properties of porcelain produced using this method were evaluated and porcelain powder and model investments suited for this method were considered.

Porcelain powder, G-Cera Cosmotech and another material without organic binder modified from G-Cera Cosmotech were used. Refractory models were filled to excess with these dry materials and sealed, and press molding was conducted by the CIP method at pressures of 100, 200, 300 and 400MPa. After correction of shape, they were fired at 970C. For comparison , samples, fired after press of 0MPa (finger pressure) and after condense (condense method) were prepared. Firing contraction, density, Vickers hardness and bi-axial flexural strength were measured for the samples. To select the powder and model investments suited for this method, the effects of varying amounts of silica added to the powder on the firing temperature and contraction, the effects of CIP pressure on the refractory model prepared with different concentration of colloidal silica was used as a mixing liquid, and change in size of the refractory model at each stage were all measured to investigate the ultimate size adaptability. (Japanese)

Dental Applications of Acoustic Emission Technique

S. Kondo, S. Ohkawa, M. Uo,T. Sugawara & F. Watari

Hokkaido J. of Dental Association, **18**(2), 73-84 (1997)

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. This article is divided into two sections. Section One includes the origins of AE generation, application to non-destructive inspection of AE, characteristics of AE parameters. Section Two deals with the recent applications to dental materials science, especially the evaluation of structural bonding of composite resins to human enamel and dentin and the differences in AE characteristics of PMMA-MMA-based and engineering plastics-based denture base materials. (Japanese)

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

S. Kondo, S. Ohkawa, M. Uo, T. Sugawara & F. Watari

J, Dent. Res. **76**(Special Issue), 315 (1997)

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. MMA was purified by conventional procedure and the middle fraction was collected. Collagen Type I (SIGMA Chemical Co.) was used without further purification. Reagent grade materials of ammonium ferric sulfate(AFeSul) , ferric bromide(FeBr),ferric chloride(FeCl), ferric citrate(FeCit),ferric phosphate(FePos) and ferric sulfate(FeSul) and ferric compounds and N-phenylglycine(NPG) were used all without further purification. Typical composition contained collagen 0.1g, ferric compound 1×10^{-4} mol,NPG 1×10^{-3} mol,MMA1.0 ml and distilled water 5.0 ml.The polymerization was carried out for various reaction periods at different temperatures and various ferric compounds/NPG ratios under air atmosphere. Percent grafting=(grafted collagen after Soxlet extraction - collagen)/collagen *100

% efficiency=(grafted collagen - collagen)/MMA*100.Results performed at 37℃ for 3 hrs are shown in the following table.

Ferric compound	AFeSul	FeBr	FeCl	FeCit	FePhos	FeSul
% Grafting	19	3	7	21	18	11
%Efficiency	2.01	0.32	0.74	2.22	1.91	1.17

Grafted collagen was characterized by FTIR spectroscopy. Grafting has been found to increase steadily with time without FeBr and FeCl served as a chain transfer agent for initial stage.FeCit-NPG redox initiator showed maximum grafting. (English)

Fracture Toughness of Acrylic Heat-Cured Denture Base Materials Modified with Macromonomer

S. Kondo, S. Ohkawa, M. Uo, T. Sugawara & F. Watari

J. Jap. Dent. Mater. Dev., **16**(Special Isuue 29), 88 (1997)

Macromonomer having polymerizable methacryloxyl group in high molecular weight monomer copolymerize with various vinyl monomers and the graft polymers obtained show the advanced performance due to the difference of segment component and graft component.The objective of this study was to examine the effect of macromonomer on fracture toughness of PMMA-MMA based denture base resin. AA-6(segment component-PMMA and graft component-methacryloxyl group) and AN-6 segment component-polystyrene and graft component-methacryloxyl group) were used as macromonomer. Fracture toughness test were carried out using compact tension specimen according to ASTM E 399-1983.

PMMA/AA-6	100/0	95/5	90/10	85/15	80/20
Fracture toughness Mean(SD) MPam$^{1/2}$	1.766 (0.127)	1.817 (0.363)	1.758 (0.241)	1.435 (0.093)	1.373 (0.183)

PMMA/AA-6	100/0	95/5	90/10	85/15	80/20
Fracture toughness Mean(SD) MPam$^{1/2}$	1.902 (0.249)	1.456 (0.140)	1.255 (0.045)	1.085 (0.045)	1.156 (0.019)

Fracture toughness of the materials modified with AA-6 showed the maximum value at PMMA/AA-6=95/5 (% by wt.). But fracture toughness of the materials modified with AN-6 decreased gradually with increasing the AN-6 contents of PMMA-AN-6 ratio. (Japanese)

Mechanical Properties and Processing Shrinkage of PMMA-MMA-Based Denture Base Resins Modified with Expansible Spherical Filler

S. Kondo, S. Ohkawa, M. Uo, T. Sugawara & F. Watari

J. Jap. Dent. Mater. Dev. 16(Special Issue 30), 85 (1997)

The objectives of this study were to measure the processing shrinkage and bending properties of PMMA-MMA based denture base resin modified with thermal expansible spherical filler(Expancel 642WU).
Bend test was carried out according to ISO 1567-1978.

E642WU/PMMA	0/100	5/95	10/90	15/85	20/80
Bend strength kgf/mm^2	6.96 (0.93)	7.55 (0.64)	7.27 (0.62)	6.99 (0.45)	5.91 (1.31)
Elastic modulus kgf/mm^2	227.2 (22.53)	236.61 (4.34)	216.46 (9.16)	216.92 (1.89)	207.39 (5.98)

The material modified with Expancel 642WU under 20 % by wt showed slightly higher bend strength and lower elastic modulus as compared with no-modified material. Both of the bend strength and elastic modulus attained to their maximum values for loading 5% by wt. and beyond this loading they gradually decreased. (Japanese)

Reaction of Titanium with KHF_2-LiF-NaCl-KCl Fluxes for Soldering

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The cumulutive weight losses of titaium plates when they were immersed in six KHF_2-LiF-NaCl-KCl fluxes were measured to examined the reaction of titanium. Spreading areas of a silver solder were determined using these fluxes. The cumulutive weight losses of titaium increased with the increasing immersion times at 900℃ for all fluxes. 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 temperature also affected the reactivity. The activation energy was 19.5 kcal/mol in the initial reaction brtween and (56KHF_2-14LiF-30(NaCl+KCl)). The spreading areas of solder increased in the order of (NaCl), (70KHF_2-30LiF)<(KHF_2)<(50KHF_2-50LiF), (56KHF_2-14LiF-30(NaCl+KCl)), except LiF. The spreading of solder hardly ocurred for LiF. The reactivity of the fluxes was not alway consistent with the increasing in the spreading areas of solder. (Japanese)

AgCl-LiF-KHF_2 Fluxes for the Soldering of Titanium

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The purposes of this study are to examine the deposit of an Ag film on titanium in AgCl-LiF-KHF_2 fluxes, to measure the joint strengths of titanium and to analyze the metallography of the joint areas. The compositions of fluxes were 100AgCl, 90AgCl-10LiF, 90AgCl-10KHF_2, 85AgCl-10LiF-5KHF_2, 9.1AgCl-54.5LiF-36.4KHF_2. Ag deposits were observed more easily when a flux mixtures, rather than single flux AgCl,was used. The most satble and extensive deposits were obtained with 85AgCl-10LiF-5KHF_2. The diffusion zone of Ag to the base were 8 to16 μm. Joint strengths (MPa)were 148.9 (±79.3), 97.4 (±27.9), 259.4(±105.7) for Ag solder, 16K gold solder, Ti-Ni-Cu solder respectively , using 85AgCl-10LiF-5KHF_2. Metallurgical structures of the joints areas were composed of multi-phase for all solders. These were influence by complicated reaction of the solders with fluxes including the base. Titanium was dissolved in Ag solder and 16K gold solder. In the case of Ti-Ni-Cu solder, Ag deposition was found not only at the boundary between the base and the solder, but also in the interior of the joint. Although the overall results of soldering were not completely satisfactory, some degree of Ag deposition was produced by the fluxes tested in this study, as was reported by DeCecco et al. The control of soldering defect and metallurgical structures is essential for good soldering performance. Further modification of the fluxes is needed to improved the soldering of Titanium.
(English)

Preparation and optical properties of amorphous silica doped with porphins, TCPP

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Tetrakis(4-carboxyphenyl)porphine (TCPP), which is well known as a photochemical hole burning(PHB) dye, was incorporated in amorphous silica materials(a-SiO_2) by a sol-gel process with using tetramethoxysilane(TMOS) and aminopropyltriethoxysilane(APTES). With using APTES as precursor of silica gel, TCPP was cross-linked to a-SiO_2 matrix through aminopropyl group of APTES. The cross-linkage of TCPP and APTES was confirmed by the FT-IR measurement. The TCPP incorporated in a-SiO_2 matrices showed activity in PHB. In the TCPP cross-linked a-SiO_2, properties of photochemical hole, such as hole width, quantum efficiency and irreversible broadening under cycle annealing experiment, were improved. A burnt hole at 3.6K was observed after cycle annealing experiment up to 80K in the TCPP cross-linked a-SiO_2. (English)