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CORROSION ENGINERRING LABORATORY

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H. Imai, K. Imasawa, M. Ishida, T. Miyano, Y. Tanaka,

Dr. Notoya attended the 8th European Symposium on Corrosion Inhibitors at Ferrara, Italy, in September, and also attended the Australasian Corrosion Association Meeting, Corrosion & Prevention 95, at Perth, Australia, in November.

Researches in progress are as follows.

(1) To save energy in producing pure aluminum from scrap aluminum, an electrochemical cycle system has been developed. The electrochemical characteristics of the three-phase electrolysis system for recycling of scrap aluminum, one component step of the system, is under study at about 750℃ and about 200℃. The characteristics of active areas for reduction of chlorine in an aluminum-chlorine chemical cell, other component step of the system, is also under investigation.

(2) For electrorefining of Al from scrap aluminum by using a bipolar electrode system, the available molten salts predominantly composed of chloride were developed. The anodic dissolution characteristics of Al-Cu alloys are being investigated in the melts together with the effect of cell materials on the reaction.

(3) The morphology and the electrochemical characteristics are being studied inco-deposition of titanium and manganese with aluminum in low-temperature chloride melts containing $AlCl_3$.

(4) Corrosion behavior of the aluminum layers electrodeposited from room-temperature molten salt baths is being studied in tap water by electrochemical techniques.

(5) In relation to the corrosion of electronic circuits, electrochemical investigations of several compositions of tin-lead alloys in sulfuric acids are in progress. The effect of chlorine ions on their corrosion rates is also under investigation.

(6) Surface layers initially produced on copper and iron in nitrogen or air containing sulfur dioxide and water vapor are being investigated by *in situ* techniques, such as IRAS and QCM.

(7) The mechanisms of inhibition action of newly-developed benzotriazole related compound are been explored for copper and copper alloys using electrochemical and optical techniques. The effect of heat treatment of copper on unusual localized corrosion, "Ant's Nest Corrosion", in copper pipes is being studied under simulated conditions in order to understand its mechanism and to prevent entirely this type of corrosion in heat transfer units. Case studies of this corrosion has also been investigating.

(8) Investigation into electrode/electrolyte interfaces at gold polycrystalline electrodes by spectroscopic and electrochemical techniques continues.

Presentations

Evaluation of Corrosion Resistivity of Al-Electrodeposits in Tap Water ; S. Kobayashi, S. Konda, T. Sasaki and T. Ishikawa : The 1995 Joint Meeting of Hokkaido Branches of Electrochemical, Corrosion Engineering and Surface Finishing Socs. Jpn., Sapporo, Jan., 1995.

Anodic Dissolution Characteristics of Al-Cu Alloys in a $BaCl_2$-$NaCl$-AlF_3-NaF Molten Salt Systems ; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa ; *ibid.*

Measurements of the Electric Double Layer Capacity at Gold

Polycrystalline Electrode/Electrolyte Interfaces ; S.Hara, T. Sasaki and T. Ishikawa : *ibid.*

In situ Measurements of the Initial Stage of Atmospheric Corrosion ; T. Sasaki, T. Itoh and T. Ishikawa : The Winter Meeting of Hokkaido Section of Jpn. Inst. Metal, Muroran, Jan., 1995.

The SERS Spectra of Benzotriazole and Related Compounds on a Copper Electrode in 2M Sulfuric Acid ; A.R. Trueman, T. Notoya and D. P. Schweinsberg : 1st Australian Conference on Vibrational Spectroscopy, Sydney, Australia, Feb., 1995.

Electrochemical Formation of Cu(I)-Benzotriazole Films on Copper Electrodes and the Mechanisms of Copper Corrosion in Chloride Solutions Containing Benzotriazole ; T. Notoya, A. D. Modestov, G. D. Zhou, Y. P. Wu and D. P. Schweinsberg : The 67th Spring Meeting of Jpn. Chem. Soc., Kyoto, March, 1994.

Anodic Dissolution Characteristics of Al-Cu Alloys in the Melts for Electrorefining of Aluminum ; The 62nd Meeting of Electrochem. Soc. Jpn., New Development of Industrial Electrolysis, Tokyo, April, 1995.

In situ IR-RAS measurements of Initial Corrosion Layers Formed on Copper in Atmospheric Corrosion Environments ; T. Itoh, T. Sasaki and T. Ishikawa : 95 Spring Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1995.

IR Spectra of Water Layers Formed on Copper and Gold in the Atmosphere ; J. Itoh, T. Sasaki and T. Ishikawa : *ibid.*

In situ Simultaneous Measurements Using IR Spectroscopy and QCM ; T. Sasaki, T. Itoh, J. Itoh, K. Noda, M. Seo and T. Ishikwa : *ibid.*

Corrosion and Prevention of Copper and Copper Alloys ; T. Notoya : The 1995 Annual Memorial Meeting of Japan Rust Prevention Association, Tokyo, July, 1995.

Reaction Properties of Al-Ti Co-deposition in Low-temperature Molten Salts Containing $AlCl_3$; N. Ohya, S. Konda, T. Sasaki and T. Ishikawa : The Summer Meeting of Hokkaido

Section of Jpn. Inst. Metal, Muroran, July, 1995.

Anodic Polarization Behavior of Al-Cu Electrodes in AlF_3-NaF-$BaCl_2$-$NaCl$ Molten Salts ; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa : *ibid.*

Development of a Reference Electrode for an AlF_3-NaF-$BaCl_2$-$NaCl$ Molten Salt System ; H. Nakamura, M. Ueda and T. Ishikawa : *ibid.*

Benzotriazole-Monoethanolamine as Corrosion Inhibitor for Copper Dissolution in Chloride Solutions ; T. Notoya and T. Ishikawa : *ibid.*

Inhibition Effect of Benzotriazole-Monoethanolamine Salt on Copper Corrosion ; T. Notoya, N. Sugii and T. Yamaguchi : The 15th Meeting of Japan Rust Prevention Association, Tokyo, July, 1995.

Synergistic Effects of Benzotriazole and Monoethanolamine on Corrosion of Copper ; T. Notoya and T. Ishikawa : The 1995 Summer Meeting of the Hokkaido Section of Chem. Soc. Jpn. Hakodate, July, 1995.

Development of an Al-Cl_2 Chemical Cell for Production of $AlCl_3$; T. Ishikawa : The 95 Fall Meeting of Electrochem. Soc. Jpn., Physical Properties of Molten Salts and Development of New Materials in the Salts, Kouhu, Sep., 1995.

Effects of Cell Materials on Polarization Behavior of an Aluminum Electrode in Chloride Melts Containing AlF_3 ; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa : *ibid.*

Effects of Chlorine Ions on Corrosion Behavior of Tin-Lead Solder in Sulfuric Acids ; T. Sasaki, C. Han and T. Ishikawa : The 42nd Discussion Meeting of Jpn. Soc. Corros. Eng., Sapporo, Sep., 1995.

Corrosion Protection of Thin-Walled Beryllium Copper Bellows for a Water-Cooled Super Computer with Benzotriazole ; T. Notoya, H. Hamamoto, K. Katsuyama and M. Miyo : The 8th European Symposium on Corrosion Inhibitors, Ferrara, Italy, Sep., 1995.

Modern FT-Raman Spectrometers and Their Application to the

Study of Corrosion Inhibition; T.G. Hope, V. Otieno-Alego, D. P. Schweinsberg and T. Notoya : The Australasian Corrosion Association Meeting, Corrosion and Prevention 95, Perth, Australia, Nov., 1995.

Corrosion Inhibition of Copper with Benzotriazole and its Amine Salts ; T. Notoya : The 35th Meeting of Japan Copper and Brass Research Association, Osaka, Nov., 1995.

On the Electrode Materials for Chlorine Reduction in an Al-Cl_2 Chemical Cell in Low-Temperature Molten Salt Systems ; S. Konda, T. Sasaki and T. Ishikawa : The 27th Meeting of Molten Salt Chemistry, Yokohama, Nov., 1995.

Co-deposition Reaction of Al-Ti in Low-temperature Molten Salts Containing $AlCl_3$; N. Ohya, S. Konda, T. Sasaki and T. Ishikawa : *ibid.*

Development of a Reference Electrode in Low-Temperature Molten Salts Containing AlF_3 ; H. Nakamura, M. Ueda, and T. Ishikawa : *ibid.*

Effects of Cell Materials on Anodic Polarization Behavior of Al-Cu in Low-Temperature Molten Salts Containing AlF_3 ; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa : *ibid.*

In situ IRAS-QCM measurements of Surface Layers Formed on Metal in Corrosive Gas Environments ; T. Ishikawa and T. Sasaki : 95 Symposium on Corrosion Measurement, Tokyo, Nov., 1995.

MATERIALS CHARACTERIZATION CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Prof. Dr. H. Tamura,
Res. Assoc. I. Saeki, and Secretary T. Komine

Students

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K. Mita, I. Sugiyama, A. Tanaka, and J. Sedaka

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

Dr. Tamura joined The 1995 International Conference on Ion Exchange, Takamatsu, in Dec.

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 can be two incorporation processes : a faster surface reaction and a slower bulk reaction.

(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 industry and natural environments. From a model analysis, it was found that the acid-base, charge, and ion adsorption characteristics of Al_2O_3, Fe_2O_3, Fe_3O_4, TiO_2, and MnO_2 surfaces can be explained with the electronegativity of oxide lattice metal ions. However, SiO_2 showed a deviation from the correlation.

(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 the concentration of EDTA species and the transfer of lattice oxide ions by proton attack. Oxyen oxidizes Fe(II)-EDTA, a dissolution product, to Fe(III)-EDTA chelate, and decreases the dissolution rate due to the loss of the Fe(II)-EDTA chelate as a dissolving agent.

(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. (a) Breakaway oxidation occurred when the film thickness attained a critical thickness which is different with atmosphere. (b) Breakage of the initially grown protective oxide film initiated before breakaway oxidation but broken part was cured itself. (c) 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

Modeling of the Dissolution of Magnetite in Chelating Agent Solutions for Chemical Decontamination of Nuclear Power Plants : The 1995 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Surface Finish. Soc., and Corros. Eng. Soc., Sapporo, Jan., 1995.

Model Evaluation of Ion Exchange Properties of Resin Carboxyl Groups ; H. Tamura and R. Furuichi : The 1995 Winter Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1995.

Correlation between the Co(II) Ion Adsorption Ability of Metal Oxides and the Electronegativity of Lattice Metal Ions Evaluated by Modeling ; H. Tamura, N. Katayama, and R.

Furuichi : The 69th Spring Annual Meeting of Chem. Soc. Jpn., Kyoto, Mar., 1995.

On the Initial Oxide Film Properties Formed on Stainless Steel Surface at Elevated Temperatures ; I. Saeki, T. Saito, H. Konno and, R. Furuichi : 1995 Annual Meeting of JSCE, Sapporo, Apr., 1995.

Characterization of the Ion Exchange Ability of Surface Hydroxyl Groups on Metal oxides Evaluated by Modeling ; H. Tamura and R. Furuichi : The 56th Symposium on Anal. Chem., Osaka, May, 1995.

Initial Oxidation of SUS 304 Stainless Steel in O_2-N_2 Atmosphere at 1273 K ; I. Saeki, T. Saito, H. Konno, and R. Furuichi : JSCE CORROSION '95, Tokyo, May, 1995.

Modeling and Evaluation of Acid-Base and Charge Characteristics of Fe_2O_3 and SiO_2 Particle Surfaces ; K. Mita, H. Tamura, and R. Furuichi : The 1995 Summer Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Hakodate, Jul., 1995.

Modeling and Evaluation of Co^{2+} Ion Adsorption Ability of TiO_2 Particle Surfaces ; T. Abe, H. Tamura, and R. Furuichi : ibid.

Photo-Electrochemical Responce of TiO_2-WO_3 Mixed Oxide Films Formed by Thermal Oxidation ; I. Saeki, N. Okushi, and R. Furuichi : Hokkaido Branch of JIM Summer Meeting, Muroran, Jul., 1995.

Initial Oxidation of SUS 430 and 304 Stainless Steel in O_2-N_2 Atmosphere at 1273 K ; I. Saeki, T. Saito, H. Konno and, R. Furuichi : Hokkaido Branch of JIM Summer Meeting, ibid.

Effects of pH and Oxygen on the Dissolution Rate of Magnetite in EDTA Solutions ; S. Takasaki, K. Ogura, H. Tamura, and M. Nagayama : The 42nd Jpn. Corros. Conf., Sapporo, Sept., 1995.

Rate of Li Ion Incorporation into Spinel Type Manganese Oxide ; A. Tanaka, H. Tamura, and R. Furuichi : The 44th Annual Meeting of Anal. Chem., Sapporo, Sept., 1995.

Modeling of Ion Exchange Properties of Metal Oxide Particle Surfaces ; H. Tamura : SRL Forum on Anti-corrosion Properties of Precipitate Type Films on Steel (Jpn. Steel Co.), Futtsu, Sept., 1995.

A Model of the Dissolution Rate of Magnetite (Fe_3O_4) in Deaerated EDTA Solutions ; H. Tamura, S. Takasaki, and R. Furuichi : The 48th Symposium on Colloid and Surf. Chem., Sapporo, Oct., 1995.

Formation of Transient Metal-Titanium Composite Oxide Film and Its Photo-electrochemical Properties ; N. Okushi, I. Saeki, and, R. Furuichi : 92nd Meeting of SFSJ, Kitakyusyu, Oct ., 1995.

Modeling of Ion Exchange Properties of Carboxyl Sites Distributed in Resin Pores ; H. Tamura and R. Furuichi : International Conf. of Ion Exchange, Takamatsu, Dec., 1995.

NUCLEAR REACTOR MATERIALS LABORATORY

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The current research activities of the laboratory are mainly concerned with corrosion of metallic materials used in nuclear industry, development of fuel cell using hydrogen reservoir alloys, estimation of pitting corrosion, migration of noble metal fission products in UO_2, thermal properties of cesium uranates, and radioactive waste management.

(1) Relationships between kinetics of hydrogen absorption by electrolysis and hydrogen concentration profiles of Ti and Zr were investigated by a nuclear chemical and other conventional techniques. Hydrogen atoms interact very intensively with each others 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.

(2) Processes of passivation and localized corrosion of metals were studied by 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. These data are divided into two direct and

alternate components. The alternate component can be calculated and changed into a frequency spectrum by maximum entropy method. The spectrum shape was expressed as the slope and magnitude. The shapes of the spectra during the corrosion were expressed by the relationship of $I=F^n$ $(-1 \leqq n \leqq 0)$ in the range of frequency from 10^{-2} to 10 Hz. The method was applied for estimate of the stability of passive films in a solution, connecting with a relationship between film displacement and corrosion current. We can finally obtain the possibility for the prediction of the pit generation.

(3) Pd is the most corrosive noble metal fission product against SiC in coated particle fuels for high temperature gas-cooled reactors. To clarify the effects of Pd on the fuel performance, the migration behavior of Pd in uranium dioxide pellets has been studied. Penetration profiles of Pd in the pellets were obtained by the electron probe microanalysis. Diffusion coefficients of Pd in UO_2 were decided at temperatures from 1600 to 2100K. The diffusion coefficients were in the order of 10^{-15} m²/s, though the vapor pressure of Pd is 10^{-3} torr at 1700K. In an attempt to clarify the migration process of Pd, the evaluation of several migration processes was carried out.

(4) 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 decided 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 conductivities 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 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 anticipate that the temperature of UO_2 fuel appreciably rises,

when $Cs_2U_2O_7$ forms in the periphery of UO_2 pellets.

(5) The corrosion behavior of overpack materials in bentonite was studied for safety assessment of the geological disposal of the high level radioactive waste. Average corrosion rates of iron and apparent diffusion coefficients of corrosion products were determined, using neutron-activated iron foils and bentonite specimens with different dry densities. The corrosion rates and diffusion coefficients depended on dry density of the bentonite. Quantitative analysis of the corrosion products was also made using 1,10-phenanthroline as a colorimetric indicator to obtain the concentration 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 would be changed by corrosion of iron.

(6) In connection with the long-term prediction of the migration behavior of radioactive nuclide in compacted bentonite, the vapor pressure of water in bentonite (Kunigel- V1) was measured as functions of water content and temperature, under an external pressure free condition. Relative partial molar Gibbs free energy $\Delta G(H_2O)$, enthalpy $\Delta H(H_2O)$ and entropy $\Delta S(H_2O)$ of the water were determined at temperature of 298.15 K. Interlayer distance of montmorillonite in bentonite was found to be 3 water layers at water content of 20.3wt% by the X-ray diffraction method. One third of the water in bentonite at the water content is similar to the ordinary water, but is not regarded as dilute electrolytic solutions. One fourth of the total water of bentonite at the water content is bound ; the relative partial molar entropy of the water is from the full to a half of the entropy of solidification of water. The thermodynamic quantities are considered to be dependent on pore water, interlayer water in montmorillonite and adsorbed water on other minerals as a function of water content. In addition, to clarify the kinetic properties of water in bentonite, diffusion of

tritiated water and argon in compacted bentonite have been studied as a function of temperature and dry density by the liquid scintillation counting and mass spectrometric methods.

(7) 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 pulverized granitic rock and kaolinite were measured by a batch method as a function of contact time, pH, and the concentrations of Sr^{2+} and humic acid.

Presentations

Safety Assessment of Geological Disposal of High-Level Radioactive Waste ; S. Sato ; Hyosetsu Seminar held by Hokkaido Branch of The Japan Society for Analytical Chemistry, Otaru, Jan., 1995

A View on the Radioactive Waste Disposal ; H.Ohashi, Simposium at Research Laboratory for Nuclear Reactors, Tokyo Institute of Technolgy, Tokyo, Feb., 1995.

Oxidation of Pyrite in Bentonite during Drying; H. Tamai, T. Kozaki, S. Sato, H. Ohashi; The 1995 Annual Meeting of the Atomic Energy Society of Japan, Tokyo, March, 1995.

Effect of Humic Acid on Sorption of Sr(II) onto Kaolinite ; Y. Niitsu, M. Samadfam, S. Sato, H. Ohashi ; The 1995 Annual Meeting of The Atomic Energy Society of Japan, Tokyo, March, 1995.

Chemical Interaction of Humic Acid with Sr(II) ; M. Samadfam, Y. Niitsu, S. Sato, H. Ohashi ; The 1995 Annual Meeting of The Atomic Energy Society of Japan, Tokyo, March, 1995.

Redistribution of Cations Induced by Corrosion of Iron in Compacted Bentonite ; T. Kozaki, H. Tamai, S. Sato, H. Ohashi : The 1995 Annual Meeting of the Atomic Energy Society of Japan, Tokyo, March, 1995.

Control of Excess Heat Evolution for Solid State of Proton Conductor in High Temperature Deuterium Gas ; T. Mizuno ; The 12th Meeting for Nuclear Reaction in the Solid State, Osaka, April, 1995.

Analysis of Elements for Solid State Electrolyte in Deuterium Atmosphere during Applied Electric Field ; T. Mizuno ; International Conference of a Low Temperature Transmutation, Texas A & M University, College Station, USA, June, 1995.

Excess Heat Evolution and Analysis of Elements for Solid State Electrolyte in Deuterium Atmosphere during Applied Electric Field ; T. Mizuno ; Conference of A Low Temperature Nuclear Fusion in Solid State, Minnesota University, Mineapolice, USA, June, 1995.

Relationship Between Excess Heat Evolution and Changes of Elements for Solid State, Electrolyte in Deuterium Atmosphere during Applied Electric Field ; T. Mizuno; Meeting of A Cold Nuclear Fusion in Solid State Stanford University, Menlo Park City, USA, June, 1995.

Anomalous Heat Generation and Reaction Products From a Solid State Electrolyzed in Deuterium Gas ; T. Mizuno ; 2nd Work Shop for New Hydrogen Energy, Tokyo, July, 1995.

Geological Disposal of High-Level Radioactive Waste in European Countries, The Present Status of Safety Assesment ; S. Sato : 1995-Meeting of Association of Chemical Education in Hokkaido, The Hokkaido Branch of The Chemical Society of Japan, Hokkaido University, Sapporo, July, 1995.

Effects of Oxidation of Pyrite on Corrosion of Iron and on Migration of Corrosion Products in Bentonite ; T. Kozaki, H. Tamai, S. Sato, H. Ohashi : The 42nd Annual Meeting of Japan Society of Corrosion Enginnering, Sapporo, September, 1995.

Effect of Surface Hydride Layer on the Hydrogen Absorption Reaction by Electrolysis of Ti ; T. Mizuno and M. Enyo ; The 42nd Annual Meeting of Japan Society of Corrosion

Engineering, Sapporo, September, 1995.

Diffusion of Sodium Ions in Compacted Sodium Montmorillonite ; A. Fujishima, T. Kozaki, S. Sato, H. Ohashi : The 1995 Fall Meeting of the Atomic Energy Society of Japan, Tokai-mura, Oct., 1995.

Thermal Expansion and Thermal Diffusivity of Cesium Uranates ; K. Takano, S. Sato, H. Ohashi, K. Minato and K. Fukuda ; The 1995 Fall Meeting of the Atomic Energy Society of Japan, Tokai-mura, Oct., 1995

Molecular Weight Distribution of Np(V)-Humate ; Y. Sakamoto, S. Nagao, S. Sato, H. Ohashi, T. Ohnuki and S. Muraoka ; The 1995 Fall Meeting of The Atomic Energy Society of Japan, Tokai-mura, Oct., 1995.

Effects of Humic Acid on Np(V) Sorption on Kaolinite and Manganese Dioxide ; Y. Niitsu, Y. Sakamoto, S. Nagao, T. Ohnuki, S. Sato, H. Ohashi and S. Muraoka ; The 1995 Fall Meeting of The Atomic Energy Society of Japan, Tokai-mura, Oct., 1995.

Clay Minerals as Barrier for Nuclide Migration; H.Ohashi, Symposium at Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo, Oct, 1995.

Basis of Nuclear Power Generation and 1ts Current Topics ; H. Ohashi. Special Lecture in Asahikawa Region of Japan Chemical Society, Nov., 1995.

INTERFACIAL ELECTROCHEMISTRY LABORATORY

Prof. Dr. M.Seo, Assoc. Prof. Dr. K. Azumi, Res. Assoc.
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K. Suzuki, G. Yamamoto, S. Morishita

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, surface finishing.

(1) Piezoelectric Detection of Difference in Contact Adsorption of Iodide and Bromide Ions on Gold Electrode

The difference in contact adsorption of iodide and bromide ions on gold in deaerated 1.0 M $NaClO_4$ solutions was investigated by a piezoelectric detection of changes in surface energy. The negative shift of pzc of gold due to addition of bromide ions was not significant as compared with that due to addition of iodide ions, indicating the strong contact adsorption of iodide ions rather than bromide ions. It was found from the iodide and bromide concentration dependences of pzc that the Esin-Markov relation held at pzc for both ions.

The piezoelectric signals at the high potentials far from pzc suggested the possibility of structural changes or phase changes of iodine and bromine adlayers which would lead to monolayer formation of surface compounds with sign-reversal of total surface charge density.

(2) Effects of Electrochemical Etching Conditions on Microstructures, Chemical Compositions and Luminescence Properties of Porous Silicon Layer

Porous silicon layer (PSL) was prepared on single crystal p-type Si (100) wafers under different electrochemical etching conditions in HF aqueous solutions to make clear the relation between microstructures, chemical compositions, and luminescence properties of PSL. The surface morphology, microstructure, and surface chemical species of PSL were observed with SEM and TEM, and identified with FT-IR, respectively.

The intensity of visible photoluminescence (PL) emitted from PSL increased with increasing the current density of electrochemical etching. The PSL consisted of dispersed ultra-fine Si particles with a diameter of 2 - 5 nm. The surface SiHx concentration of PSL, however, decreased with increasing the current density. From these results, it is concluded that the quantum confinement effect is operative on the visible luminescence and surface compound, SiHx forms the surface states to reduce the luminescence intensity.

(3) Corrosion Behavior of Iron Thin Film in Deaerated Phosphate Solutions

The quartz crystal microbalance (QCM) technique was applied to evaluate the corrosion behavior of electroplated iron thin film in deaerated 0.3 M phosphate solutions of pH 6.48, 8.48, 10.48, and 12.48. The mass of the film at natural immersion decreased linearly with time in pH 6.48 and 8.48 phosphate solutions, which resulted from dissolution of iron as ferrous ions. The corrosion rate of the film was almost same in pH 6.48 and 8.48 solutions. The circulation and aeration of solutions promoted the corrosion.

The mass of the film increased gradually with time in pH 10.48 and 12.48 solutions, which was mainly attributed to deposition of corrosion products such as $Fe(OH)_2$ and $Fe_3(PO_4)_2$.

(4) Observation of Changes in Surface Morphology of Carbon Steels Subjected to Corrosion in Deaerated Carbonate Solutions

The changes in surface morphology of carbon steel subjected to corrosion in deaerated 0.1 M and 1.0 M carbonate solutions of pH 9.8 with and without 10^{-2} M chloride ions at 35 ℃ were observed with SEM and Phase Detection Interferometric Microscope (PDIM) to evaluate the corrosion heterogeneity of carbon steel. The carbon steel surfaces subjected to active dissolution in 0.1 M carbonate solution were covered with corrosion products. On the other hand, the major parts of carbon steel surface subjected to active dissolution in 1.0 M carbonate solution were free from corrosion products and the surface roughness increased with increasing the amount of corrosion.

The addition of chloride ions in the solutions suppressed the increase in surface roughness to some extent. The changes in surface morphology of carbon steel due to corrosion were quite different in pearlite and ferrite phases.

(5) Construction of Scanning Electrochemical Microscope for Evaluation of Heterogeneity of Passive Films

Scanning Electrochemical Microscope (SECM) was constructed to evaluate the heterogeneity of passive films on metals. In principle of SECM, a redox system is introduced into solution to induce the forward redox reaction preferentially at the defective sites of passive films on metals and the backward redox reaction current is measured with a scanning probe electrode consisting of Pt wire of dia. 5 μm. The heterogeneity of passive films formed on iron and titanium in borate solution is now being examined with SECM.

(6) Change in Electronic Property of the Titanium Oxide Film in Deaerated Neutral Solutions

To evaluate the stability of oxide layer on titanium under deaerated aqueous environment, change in electric property of the oxide film anodically formed on titanium electrode was followed by impedance measurement in pH 8.4 borate and pH 9.9 carbonate solutions for 32 h under potential control around the immersion potential region. Three kinds of variation in electric property of the oxide film were observed, i. e., decrease of electric resistivity due to hydrogen absorption at lower potential, generation / degeneration of surface states which formed at higher anodic potential, and slow decrease of electric resistivity near the immersion potential which seems to concern with hydration of the oxide film.

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

For well understanding the mechanism of double zincate process pre-treatment for plating on aluminum alloys, SEM observation, trace of electrode potential and weight change during 1st and 2nd zincate process were conducted. Zinc particles grew during the first zincate process, on the other hand, a thin, uniform Zn layer formed during the second zincate process. We found that the difference in zinc particle nucleation between the first and second processes is related to surface morphology and thickness nonuniformities in the preexisting oxide film air-formed on the alloy.

(8) Other Activities

Dr. K. Noda moved to Prof. T. Tsuru's laboratory at Tokyo Institute of Technology on April 1st., 1995. The International Symposium on Plant Aging and Life Prediction of Corrodible Structures sponsored by Japan Society of Corrosion Engineering and NACE International was held at Hokkaido University, Sapporo, Japan on May 15 -18.

Prof. M. Seo and Mr. K. Shigyo (Ph. D. Student) attended the 187th Electrochemical Society Meeting which was held in Reno, Nevada, USA, on May and presented two papers entitled "Piezoelectric Detection of Changes in Surface Energy of Gold Electrode in Perchlorate Solutions Containing Iodide Ions" and "Surface Morphology and Electroluminescence of Porous Silicon Layer Prepared on P-Type Silicon with Electrochemical Etching in HF Aqueous Solutions". Afterward, they visited Profs. W. H. Smyrl and M. D. Ward at the Corrosion Research Center, University of Minnesota, Minneapolis, to conduct the

Collaborative Research on "Microscopic In-situ Evaluation of Corroding Surface of Film".

Prof. M. D. Ward, University of Minnesota visited this laboratory on July for the Collaborative Research and presented the lecture entitled "The Quartz Crystal Microbalance : Principle, Application, and Experimental Issues". Mr. K. Fushimi joined this laboratory as research associate on August 1st.

Prof. M. Seo visited again Prof. W. H. Smyrl at the Corrosion Research Center, University of Minnesota, Minneapolis on November to complete the Collaborative Research. Afterward, he visited Profs. R. A. Rapp and G. S. Frankel, Dept. Materials Sci. Eng., The Ohio State University, Columbus, Ohio, and Dr. J. B. Lumsden, Rockwell International Science Center, Thousand Oaks, California.

The following foreign scientists visited this laboratory : Dr. B. MacDougall, Institute for Environmental Research and Technology, National Research Council Canada, on March 8, Prof. R. C. Newman, Corrosion and Protection Centre, UMIST, UK, and Dr. P. Mayer, Ontario Hydro-technologies, Canada, on May 17, Prof. M. D. Ward, University of Minnesota, USA, on July 24 - 30, Dr. S. Lee, Dept. of Metallurgy, The University of Tokyo and Dr. U. Kamachi Mudali, Indira Gandhi Centre for Atomic Research, India, on Sept. 25, and Prof. G. E. Thompson, Corrosion and Protection Centre, UMIST, UK, on Dec. 6.

Presentations

Measurement of Changes in Surface Stress of the Metal／Solution Interface by a Piezoelectric Response Method; M. Seo : The 5th Joint Symp. of Hokkaido Secs. of JIM and ISIJ, Muroran, Jan., 1995.

Fundamental Study of Microbiologically Influenced Corrosion - Effects of Ferrous Ions on the Metabolism of Sulfate - Reducing Bacteria ; F. Baba, T. Suzuki and M. Seo : The 1995 Joint Meeting of the Hokkaido Secs. of Electrochem.

Soc., Surf. Finish. Soc., and Corros. Eng. Soc. Jpn., Sapporo, Jan., 1995.

Effect of HF Concentration on Surface Structure of P-Type Silicon Electrochemically Etched ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi : *ibid.*

Study of Contact Adsorption Behavior of Iodide Ions on Gold Electrode by a Piezoelectric Response Method ; K. Ueno and M. Seo : *ibid.*

Influence of Solution Species on Hydrogen Absorption of Palladium and Acoustic Emission ; K. Azumi, M. Seo and D. A. Stevenson : The 1995 Winter Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1995.

Corrosion Behavior of Electroplated Iron Thin Film in Neutral Carbonate Aqueous Solutions ; K. Noda, Y. Hirota and M. Seo : *ibid.*

Electrochemical Evaluation of Defects in TiN and Al_2O_3 Thin Films Prepared with PVD ; M. Koike, K. Noda, H. Takahashi and M. Seo : *ibid.*

Surface Structure and Luminescence of P-Type Porous Silicon ; M. Seo : The 4th Meeting of ARS, Tokyo, Mar., 1995.

Photoelectrochemical Behavior of TiN Thin Film ; M. Seo, S. Watanabe and K. Azumi : Discussion Meeting of CVD of Iron and Steel Inst. Jpn., Tokyo, Mar., 1995.

Measurement of Changes in Gold Electrode Surface due to Contact Adsorption of Iodide Ions by a Piezoelectric Response Method;K. Ueno and M. Seo : The 62nd. Meeting of Electrochem. Soc. Jpn., Tokyo, Apr., 1995.

Surface Structures and Luminescence Behavior of Porous Silicon Prepared with Different Electrochemical Etching Conditions ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi : *ibid.*

Evaluation of Uniform Corrosion Rate of Carbon Steel in Deaerated Carbonate Solutions ; K. Noda, Y. Hirota and M. Seo : Intern. Symp. on Plant Aging and Life Prediction of

Corrodible Structures, Sapporo, May, 1995.

Piezoelectric Detection of Changes in Surface Energy of Gold Electrode in Perchlorate Solutions Containing Iodide Ions ; M. Seo, K. Ueno and Y. Yamamoto : The 187th Electrochemical Society Meeting, Reno, Nevada, U.S.A., May, 1995.

Surface Morphology and Electroluminescence of Porous Silicon Layer Prepared on P-Type Silicon with Electrochemical Etching in HF Aqueous Solutions ; K. Shigyo, M. Seo, K. Azumi, H. Takahashi, M. Al Odan and W. H. Smyrl : *ibid.*

Effects of Ferrous Ions on Iron Sulfide Formation of Sulfate-Reducing Bacteria ; F. Baba, T. Suzuki and M. Seo : '95 Spring Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1995.

Corrosion Rates of Electroplated Iron Thin Films in Neutral Carbonate Aqueous Solutions ; K. Noda, Y. Hirota and M. Seo : *ibid.*

Resistometry and AFM Observation of Ti Thin Film Electrode ; K. Azumi and M. Seo : *ibid.*

Piezoelectric Measurement of Changes in Surface Energy of Gold Electrode due to Contact Adsorption of Iodide Ions ; K. Ueno and M. Seo : The 42nd. Discussion Meeting of Jpn. Soc. Corros. Eng., Sapporo, Sept., 1995.

Electrochemical Etching Conditions of P-Type Silicon and Formation of Porous Silicon ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi : *ibid.*

Metabolism of Sulfate-Reducing Bacteria in Tubercle ; F. Baba, T. Suzuki and M. Seo : *ibid.*

DISSIMILAR MATERIALS INTERFACE ENGINEERING LABORATORY

Prof. Dr. T. Narita, Assoc. Prof. Dr. K. Ohsasa,
Res. Assoc. H. Taumi, and Tech. Staff J . Tanaka

Students

M. Noguchi, T. Yoshioka, F. Christian, S. Hata, K. A. Zaini,
T. Toyama, R. Masumoto, T. Watanabe, M. Nakano,
T. Sugawara, T. Yamamoto, Y. Suzuki, C. Fang, T. Azuma,
E . Kojima, Y. Mizuno and T. Shinmura

Professor Narita attended the 4th International Symposium on Surface Science and Engineering held in Beijng, China at May, 1995. Professor Narita and Research Associate Taumi attended the 14th International Thermal Spray Conference, held in Kobe, Japan, at May 1995. Professor Narita attended The Golden Research Conference held in New Hampshire, USA, at July 1995. Associate Professor T. Sugawara returned at March, 1996, to Fukushima National College of Technology after finishing his visiting research period. Mr. Ishida from Kobe Steel joined our laboratory as a visiting researcher from April 1995 to March 1996.

The research programs in our laboratory are as follows :

(1) Ceramic-Metal joining

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. Zirconia-metal joining was investigated for development of SOFC.

(2) 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.

(3) High temperature nitriding of alloys

Nitridation properties of Ti-Al intermetallic compounds were investigated in nitrogen atmospheres with or without impurity oxygen.

(4) 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.

(5) 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 an galvanized layer having high corrosion resistance. The interface structure formed during dipping processes was evaluated by means of SEM, EPMA and XRD.

(6) 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.

(7) Molecular dynamics simulation of grain boundary formation

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

(8) 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. The change in structure from fine equiaxed grain to coarse columnar grain with increasing super heat of melt was reproduced by the simulation.

Presentations

Diffusional Analysis of Sulfide Scale Growth on Fe-Cr Alloys Accompanied with Intergranular Sulfidation ; S. Kawamori, M. Noguchi and T. Narita : JIM '95 Fall Annual Meeting (117th), Honolulu, Hawaii, Dec., 1995.

Measurement of Cation Distribution in Sulfide Scale on Fe-Cr Alloy ; M. Noguchi and T. Narita : The 42 nd. Discussion Meeting of Jpn. Soc. Corros. Eng., Sapporo, Oct., 1995.

Effect of Pre-Sulfidation Treatment on High temperature Oxidation of TiAl ; T. Yoshioka and T. Narita : ibid.

High Temperature Oxidation Behavior of Ultra Thick Plasma Splayed Coating ; H. Taumi, S. Nakamori, Y. Harada and T. Narita : JIM '95 Spring Annual Meeting (116th), Tokyo, May, 1995.

Mechanism of Selective Sulfidation of Titanium in TiAl Alloy ; T. Yoshioka and T. Narita : ibid.

Effect of Ni Thickness on Fracture Strength of Joint with Ni-Cu-Ti Solder ; S. Hata and T. Narita : ibid.

Corrosion Rate Constant and Cation Distribution in Fe-Cr Alloy During High Temperature Sulfidation ; M. Noguchi and T. Narita : ibid.

Molecular Dynamics Simulation of Grain Boundary Formation of α Iron ; T. Toyama, K. Ohsasa and T. Narita : ibid.

Effect of Nb Addition on High Temperature Sulfidation Behavior of TiAl ; T. Yoshioka and T. Narita : The Winter Joint Meeting of the Hokkaido Sections of JIM and ISIJ, Muroran, Jan., 1995.

Study on Fracture Strength of Ceramics-Metal Joint ; S. Hata and T. Narita : ibid.

Evaluation of Property in Vicinity of Glass-Glass Joint

Interface with Ultrasonic Microscope ; S. Nakano and T. Narita : ibid.

Study on Behavior of P Atom in Iron by Molecular Dynamics Method ; T. Toyama, K. Ohsasa and T. Narita : ibid.

Analysis of Flow Characteristic in Solid-Liquid Coexisting Zone of Alloy ; K. Ohsasa and T. Narita : ibid.

Bi Addition to Ag-Cu Solder in Ceramic-Metal Joint ; T. Sugawara and T. Narita : ibid.

Phase Structure and Concentration Distribution in Molten Aluminum Plated Stainless Steel ; J. Tanaka and T. Narita : ibid.

Wear Behavior of Tool Steel ; T. Sugawara, J. Tanaka, T. Narita, H. Takahashi, S. Kamota and M. Sakai ; ibid.

Mechanism of Inner Sulfidation in Fe-Cr and Fe-Mn Alloys ; S. Kawamori and T. Narita : ibid.

High Temperature Oxidation of Plasma Splayed MCrAlY Coatings ; H. Taumi, T. Narita, M. Nakamori and Y. Harada : JIM '95 Fall Annual Meeting (117th), Honolulu, Hawaii, Dec., 1995

Improvement in Oxidation Resistance of the TiAl Alloy by the Pre-Sulfidation Treatment ; T. Yoshioka and T. Narita : ibid.

Sulfidation Kinetics and Diffusional Analysis of Fe-Cr Alloys ; M. Noguchi and T. Narita : ibid.

Molecular Dynamics Simulation of Solidification process of Iron ; K. Ohsasa and T. Narita : ibid.

Kinetics and mechanism of Inter-Granular Sulfidation of Iron Based Alloys at High Temperatures ; S. Kawamori, M. Noguchi and T. Narita : Int. Conf. Surface and Engineering, Beijing, May, 1995

Solidification Simulation of Al-Si Alloy Ingot ; K. Ohsasa, T. Ohmi, M. Kudoh and T. Narita : The 1995 Annual Meeting of Hokkaido Section of Jpn. Foundrymen's Soc., Otaru, Jun, 1995.

Ultrasonic Micro-Spectroscopy and Sound-Elasticity of Ion

Diffused Glasses ; K. A. Zaini, K. Ishikawa and T. Narita : The 1995 Spring Annual Meeting of Jpn. Non-Destructive Test Soc., Tokyo, Mar., 1995.

Ultrasonic Micro-Spectroscopic Observation of Diffused Layer in the Vicinity of Interface of Composite Glasses ; M. Nakano and T. Narita : ibid.

Solidification Simulation of Al-Si Alloy Ingot with Consideration of Contraction Flow and Solid Deformation ; K. Ohsasa, T. Ohmi, M. Kudoh and T. Narita : The 1995 Annual Meeting (127th) of Jpn. Foundry Engineering Soc., Sapporo, Oct., 1995.

INTERFACE MICRO-STRUCTURE ANALYSIS LABORATORY

Prof. Dr. H. Takahashi, Assoc. Prof. Dr. K. Kurokawa,
and Res. Assoc. Dr. M. Sakairi

Students

Y. Li, M. Shikanai, M. Ube, F. Takashima, E . Aruga,
H. Kamada, H. Shimada, H. Houzumi, and J. Wakabayashi

Mr. Li left for China in June after his stay in Sapporo for 15 months. Dr. Sakairi joined as a research associate from Japan Atomic Energy Research Institute in October.

The research activity of the laboratory is still directed to an understanding of structure and properties of anodic oxide films on aluminum and its alloys, and the corrosion resistant materials at high temperatures.

Current topics on research are in the following :

(1) AFM and CLSM observation of the surface of aluminum with polishing and etching.

The surface of aluminum with electropolishing, chemical polishing, CrO_3/H_3PO_4 treatment, and NaOH etching was observed by atomic force microscopy, confocal laser scanning microscopy, and scanning electron microscopy. On the surface of electropolished specimens, very small scalloped shape concavities and relatively large and shallow concavities were found. On the surface of chemical polished specimens, a network structure was found, whose shape strongly depends on the crystallography of the metal substrate.

(2) Localized Ni deposition on aluminum with YAG-laser irradiation.

Aluminum specimens covered with porous anodic oxide films were immersed in Ni-plating solutions, and irradiated with a pulse YAG laser through quartz window. After laser irradiation, the specimen was cathodically polarized under potentiostatic conditions. Nickel layer was found to deposit at laser irradiated area effectively, and a fine pattern with Ni-deposited line was produced on aluminum.

(3) Formation of (Ti, Nb, Ta)/Al-composite oxide films on aluminum by the pore-filling method

Aluminum specimens covered with porous anodic oxide films were immersed in Ti^{4+}-, Nb^{5+}- or Ta^{5+} -solution, and then heated in air to deposit Ti-, Nb-, or Ta-oxide in the pore. After the heat treatment, the specimen was anodized in a neutral borate solution to fill the pores with Al_2O_3. The parallel capacitance of the Ti/Al-composite oxide films formed by the pore-filling method was larger by 30 % than that of oxide films without any oxide deposition, while the oxide films incorporated with Nb- and Ta-oxide did not show any increment of the capacitance.

(4) Formation and breakdown of anodic oxide films in neutral boric acid/borate solutions.

Aluminum was anodized galvanostatically in boric acid/borate solutions with concentrations of borate at 0, 0.005 and 0.05 M at 293 K, and also the effect of hydrothermal pretreatments in distilled water and a mono-ethylamine solution on the film formation was examined. In boric acid/borate solutions, breakdown of anodic oxide films took place at 400 - 500 V, while in the boric acid solution the formation of anodic oxide films was observed until 1180 V with growth of imperfections during anodizing. Hydrothermal treatments increased considerably the rate of increase in the anode potential during anodizing, and decreased slightly the film breakdown potential.

(5) Anodizing of aluminum covered with TiO_2 films formed by CVD.

Aluminum was initially covered with TiO_2 film by a chemical vapor deposition technique with tetra-iso-propyl titanate. The

TiO_2 covered specimens were anodized galvanostatically in a neutral boric acid／borate solution. As anode potential increases, oxide films grew, which were composed of an outer TiO_2／Al_2O_3 composite oxide layer and an inner Al_2O_3 layer. The capacitance of the composite oxide film showed to be 50 % larger than that of anodic oxide films on aluminum without TiO_2 film.

(6) Oxidation behavior of high temperature materials.

Oxidation behavior of SiO_2-forming materials such as Si_3N_4 and $MoSi_2$ at high temperatures has been investigated. The oxidation of those materials is in principle controlled by the diffusion of oxygen through a SiO_2 layer. Therefore the materials have extremely outstanding oxidation resistance, although the resistance is strongly affected by the existence of a second phase such as additives and reinforcement materials.

(7) Solid-state reactions between metals and ceramics.

The interfacial reactions in metal／ceramic (SiC) systems at high temperatures have been investigated. The reactions were grouped into three modes, (A) silicide+graphite formation, (B) silicide+carbide formation and (C) Si+carbide formation. The maximum application temperature of Fe, Co and Ni based alloys／SiC composites for a hot machinery was estimated to be about 1200K. Furthermore, the investigation in metal／Si_3N_4 systems is also in progress.

(8) Bonding of $MoSi_2$ to graphite.

As a basic research for the improvement of the oxidation resistance of C／C composite, the experiments on the bonding of $MoSi_2$ to graphite have been carried out using the spark plasma sintering equipment. The bending strength is approximately equivalent to that of graphite, and it depends on the thickness of reaction layer consisting of SiC and Mo_5Si_3.

Other activities

In October, Prof. Takahashi attended the 188th meeting of the Electrochemical Society at Chicago to present two papers entitled Localized Cu Deposition on Aluminum with Pulse YAG Laser, and Electrochemical Synthesis of Al-Ti Composite Oxide Films on Aluminum. After the meeting he visited Prof. E. Yeager, R. Savinell, B. Miller and C. Liu at Case Western Reserve University in Cleveland, and then Prof. W. H. Smyrl, R. A. Oriani, D. A. Shores, and R. Staehle at the University of Minnesota in Minneapolis.

Assoc. Prof. Kurokawa, Mr. Horibe and Mr. Ube attended International Symposia on Advanced Materials and Technology for the 21st Century which was organized by the Japan Institute of Metals and held in Honolulu, U. S. A., on December 13-15. The papers entitled "High Temperature oxidation behavior of $MoSi_2$-SiC composite" and "Interfacial reaction in joining of $MoSi_2$ to graphite by SPS method" were presented in the symposia.

Foreign researches visited the IMSA-laboratory are Dr. B. MacDougall, NRC, Canada in March, Prof. M. Ward, the University of Minnesota in July, Dr. P. Hoyer, Hahn-Meitner-Intstitut, Berlin in August, and G. Thompson, UMIST, UK in December.

Presentations

Formation of Ti/Al Composite Oxide Films on Aluminum by Pore-filling - Effect of Pore-widening - ; M. Shikanai, H. Takahashi and M. Seo : The 1995 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Surf. Finish. Soc., and Corros. Eng., Sapporo, Jan., 1995.

Local Cu Plating on Aluminum with YAG Laser Irradiation ; K. Nukui, H. Takahashi, M. Seo, M. Kawasaki and Y. Matsumi : ibid.

Interfacial Reaction Between $MoSi_2$ and Carbon Material ; T.

Horibe and K. Kurokawa : The Winter Meeting of Hokkaido Secs. of JIM and ISIJ, Muroran, Jan., 1995.

Structure of Aluminum Oxide Film and Its Application in High Technology - ; H. Takahashi : ibid.

Oxidation Behavior of $MoSi_2$ -WSi_2 Solid Solutions ; K. Kurokawa and T. Matsuoka : The 123nd Committee on Heat-Resisting Metals and Alloys, Japan Society for the Promotion of Science, Tokyo, Mar., 1995.

Effect of Pore-widening on Formation of Ti／Al Composite Oxide Film on Aluminum by Pore-Filling ; M. Shikanai, H. Takahashi, M. Seo, K. Takahiro, S. Nagata and S. Yamaguchi : The 91th Annual Meeting of Surface Finishing, Tokyo, Mar., 1995.

Formation and Breakdown of Anodic Oxide Films on Aluminum in Neutral Boric Acid／Boarate Solution ; Li Ye, K. Shigyo, H. Takahashi and M. Seo : ibid.

Cu Plating on Aluminum at Selected Area with Laser Irradiation ; K. Nukui, H. Takahashi, M. Seo, M. Kawasaki and T. Matsumi : The 62th Annual Meeting of Electrochem. Soc., Tokyo, Mar., 1995.

Oxidation Behavior of $MoSi_2$-SiC Composite ; K. Kurokawa, M. Ube and Y. Sanada : The 116th Annual Meeting of JIM, Tokyo, Mar., 1995.

High Temperature Oxidation Behavior of Si_3N_4-SiC Composite ; K. Kurokawa, E. Aruga, Y, Sato and M. Ueki : ibid.

Evaluation of Imperfections in Anodic Oxide Films on Aluminum by Pit Formation Technique with Cathodic Polarization : H. Takahashi, K. Fujiwara, F. Takashima, M. Seo, M. Al-Odan and W. H. Smyrl : Intern. Symp. on Plant Aging and Life Prediction of Corrodible Structures, Sapporo, May, 1995.

Fretting Corrosion Resistance of Metallic Materials Used in Nitric Acid of Spent Fuel Reprocessing Equipment ; M. Sakairi, K. Kiuchi and M. Kikuchi : ibid.

Dielectric Property of Ti／Al Composite Anodic Oxide Film on

Aluminum ; M. Shikanai, H. Takahashi, M. Seo, K. Takahiro, S. Nagata and S. Yamaguchi : Jpn. Soc. Corros. Eng., Tokyo, Jun., 1995.

Fretting Corrosion Resistance of Zr in 3N HNO_3 Solution ; M. Sakairi, K. Kiuchi and M. Kikuchi : ibid.

High Temperature Oxidation Resistance on Silicides and Its Subjects ; K. Kurokawa : The 22th Corrosion Seminar, Jpn. Soc. Corros. Eng., Hakone, Sep., 1995.

Structure and Dielectric Properties of Ti/Al Composite Anodic Oxide Film on Aluminum ; M. Shikanai, H. Takahashi, M. Seo, K. Takahiro, S. Nagata and S. Yamaguchi : The 1995 Summer Meeting of Hokkaido Sec. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Hakodate, June, 1995.

TEM and RBS Studies on The Structure of Ti/Al Composite Anodic Oxide Film on Aluminum ; M. Shikanai, H. Takahashi, M. Seo, K. Takahiro, S. Nagata and S. Yamaguchi : The 44th Annual Meeting of Jpn. Soc. for Anal. Chem., Sapporo, Sep., 1995.

Aluminum Surface Finishing by Micro-Electrochemistry and Laser Technique : H. Takahashi : The 6th Symp. on Micro Structure, Sponsored by Chme. Engr. Soc. Jpn., Sapporo, Sep., 1995.

Application of Laser Technology to Patterning of Aluminum ; H. Takahashi : The Promotion of Scientific and Industrial Technology and Hokkaido Foundation of the Promotion of Scientific and Industrial Technology, Hokkaido Forum on The Development of New Technology, Sapporo, Sep., 1995.

Evaluation of Anodic Oxide Film Defects on Aluminum by Cathodic Polarization Method ; F. Takashima, H. Takahashi, M. Seo, M. Al-Odan and W. H. Smyrl : The 42th Annual Meeting of J. Soc. Corros. Eng., Sapporo, Sep., 1995.

Pest in $MoSi_2$ Base Materials at High Temperatures and Its Prevention : K. Kurokawa and H. Takahashi : ibid.

Electrochemical Synthesis of Al-Ti Composite Oxide Films on Aluminum : H. Takahashi, M. Shikanai, M. Seo, K.

Takahiro, S. Nagata and S. Yamaguchi : The 188th Meeting of Electrochem. Soc., Chicago, Oct., 1995.

Localized Cu Deposition on Aluminum with Pulse YAG Laser. ; H. Takahashi, K. Nukui, M. Seo, Y. Matsumi, and M. Kawasaki : ibid.

Recent Investigation on Aluminum Surface Treatment ; H.Takahashi : Seminar at Case Western Reserve University, Cleveland, Oct., 1995.

Effect of Concentration and Temperature on Fretting Corrosion of Zr in Nitric Acid Solution ; M. Sakairi, K. Kiuchi and M. Kikuchi : Atomic Energy Soc. of Japan, Tokai-mura, Oct., 1995.

For Anodic Oxide Film Formation on Aluminum at High Potentials - High Potential Sustainable Capacitor - ; H. Takahashi, Li Yi, H. Shimada : Seminar on Environment and Materials, Sendai, Nov., 1995.

High Temperature Oxidation Behavior of $MoSi_2$-SiC Composites ; M. Ube, K. Kurokawa and H. Takahashi : The 117th Meeting of JIM, Honolulu, Dec., 1995.

Interfacial Reaction in Joining of $MoSi_2$ to Graphite by SPS Method ; T. Horibe and K. Kurokawa : ibid.

Evaluation of Uniform Corrosion Rate of Carbon Steel in Deaerated Carbonate Solutions

K. Noda, Y. Hirota, and M. Seo

Draft Proc. of Intern. Symp. on Plant Aging and Life Prediction of Corrodible Structures, **B VI 11**, 1-7 (1995)

The polarization behaviors of iron and carbon steel were investigated in deaerated carbonate solutions with different pHs with relation to the prediction of the life time of overpack materials for long term storage of nuclear wastes. Furthermore, the quartz crystal microbalance (QCM) technique was applied to evaluate the corrosion rate of iron thin film in deaerated carbonate solutions which was compared with the corrosion rate of iron and carbon steel measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The corrosion of the carbon steel in alkaline solution, proceeds with two processes of dissolution and precipitation in the active region. The degree of hydration of films formed on the iron thin film during anodic polarization in alkaline solution was determined by comparing the electric charge and mass change. The dissolution rate of carbon steel in neutral solution is 5.6×10^{-9} g cm^{-2} s^{-1} which is slightly higher than that (4.0×10^{-9} g cm^{-2} s^{-1}) of iron. (English)

A Quartz Crystal Microbalance Study of The Corrosion of Iron Thin Films in Neutral Aqueous Solutions

M. Seo, K. Yoshida, and K. Noda

Materials Science and Engineering, **A198**, 197-203 (1995)

A quartz crystal microbalance (QCM) technique is capable of detecting small mass changes in the range of ng cm^{-2} from resonant frequency changes of quartz crystal. In this study, the QCM technique combined with electrochemical measurement was applied to minute corrosion of iron thin films in deaerated neutral solutions.

The iron thin film with a thickness of 200 nm was electroplated on the gold electrode of a quartz crystal. The mass changes of iron thin films during natural immersion or galvanostatic polarization in deaerated pH 6.48 borate solution, pH 6.42 borate solution with 10^{-2} M chloride ions, pH 6.0 borate solution with 0.5 M chloride ions, and pH 6.48 phosphate solution were measured as a function of time or potential to evaluate the iron dissolution rate or iron dissolution current. The corrosion rate of iron thin film at the natural immersion increased in the order of pH 6.48 phosphate $>$ pH 6.0 borate with 0.5 M chloride ions $>$ pH 6.42 borate with 10^{-2} M chloride ions $>$ pH 6.48 borate solution.

The net current flowed through the external circuit during galvanostatic polarization near the corrosion potential was successfully separated into the iron dissolution current and hydrogen evolution current. The Tafel plots of the iron dissolution current and hydrogen evolution current were performed to evaluate the corrosion mechanism of iron thin film. The Tafel slopes of iron dissolution and hydrogen evolution thus obtained depended on the electrolyte solutions from which discussions were made on the corrosion mechanism. (English)

An EQCM Study on Corrosion of Iron Thin Film in Deaerated Neutral Solutions

M. Seo, K. Yoshida, and K. Noda

Materials Science Forum, **192-194**, 755-764 (1995)

An electrochemical quartz crystal microbalance (EQCM) was applied to investigate the corrosion behavior of iron thin film in deaerated neutral solutions. The iron thin film with a thickness of 200 nm was electroplated on the gold electrode of quartz crystal. The dissolution of iron thin film at the natural immersion in pH 6.48 borate solution was promoted by the circulation of the solution. The dissolution rate at the natural immersion was higher in phosphate solution than in borate solution in spite of the same pH value of 6.48.

The net current flowed through the external circuit during galvanostatic polarization near the corrosion potential was successfully separated into the iron dissolution current and hydrogen evolution current. The Tafel plots of the iron dissolution current and hydrogen evolution current were made to evaluate the corrosion mechanism. The difference in the corrosion mechansim between borate and phosphate solutions was discussed from the Tafel slopes.

It has been suggested that the application of EQCM to the active dissolution of iron thin film at the anodic potential far from the corrosion potential needs a caution of the deposition of corrosion products on the surface or accumulation of dissolved species near the surface. The solution analysis by ICP-atomic emission spectroscopy has revealed that the dissolution rate of iron thin film is higher than that of iron plate in both borate and phosphate solution. (English)

Effects of Ferrous Ions on The Metabolism of Sulfate-Reducing Bacteria

F. Baba, T. Suzuki, and M. Seo

Zairyo-to-Kankyo, **44**, 606-611 (1995)

Effects of ferrous ions on the growth and activity of sulfate-reducing bacteria (SRB) have been investigated by using biological and analytical technique for a better understanding of its metabolism in corrosion media with high contents of metal ions. In-situ gravimetry by quartz crystal microbalance (QCM) technique was also applied to examine the sufide-producing process in the medium.

The growth of SRB increased with increasing ferrous ion concentration up to 0.01 M and retarded above 0.01 M. In the low concentration region (0.00036 - 0.01 M) ferrous ions enhanced the growth of SRB, whereas in the high concentration region (0.03 - 0.7 M) ferrous ions gave the opposite effect due to the high osmotic pressure.

The FeS producing ability was closely related to the growth of bacteria. Therefore, it seems that SRB accelerates the corrosion of metal in the medium including 0.01 M ferrous ions. QCM technique was able to detect sensitively the amount of FeS attached on the electrode surface, which was proportional to the total amount of FeS in the medium. Thus it was found that QCM technique is powerful for monitoring the FeS producing process. (Japanese)

A Comparative Study of the Inhibitive Effect of Benzotriazole and Related Compounds on Copper Corrosion

Yi-Ping Wu, Guo-Ding Zhou and Takenori Notoya

Bulletin of Electrochemistry, **10**, [Nov-Dec], 439-441 (1994)

The inhibitive action of benzotriazole (BTA) and four related compounds on copper corrosion in a 0.5M NaCl and 0.01M $Na_2B_4O_7$ mixture over a wide pH range have been investigated by AC impedance measurements and immersion tests. BTA, Tolyl-triazole (TTA) and Bis [(1-benzotriazolylmethyl] phosphonic acid(BTA-PA) inhibit copper corrosion within the pH range from 3 to 12. Dihydroxypropylbenzotriazole (BT-GL) and 2,3-Dicarboxypropylbenzotriazole (BT-250) demonstrate their ability to inhibit corrosion within the pH range from 9 to 12. However, even within this pH range these compounds are not as effective as BTA, TTA and BTA-PA. (English)

FT Raman Spectrometers and Their Application to the Study of Corrosion Inhibition

A. Truman, V. Otieno-Alego, G. Hope, T. Notoya and
D. P. Schweinsberg

Proceedings of Corrosion and Prevention 95, Western Australia,
paper 55, 1-10 (1995)

The action of organic compounds as corrosion inhibitors is outlined and the information obtainable from coupon tests and polarisation scans is discussed. The application of surface enhanced Raman spectroscopy(SERS) to inhibitor studies is also described and recent work on the inhibition of copper in aerated acid using benzotriazole and polyvinylpyrrolidone is outlined. (English)

Corrosion Protection of Thin-Walled Beryllium Copper Bellows for a Water-Cooled Super Computer with Benzotriazole

T. Notoya, H. Yamamoto, K. Katsuyama and M. Miyo

Proceedings of the 8th European Symposium on Corrosion Inhibitors(8 SEIC), 1021-1030 (1995)

A new water cooling technology for high-speed and high-density LSI's has been developed to meet the demand for rapid increases in super computer performance. The cooling system consists of a cooling header and a flexible thermal conductor (FTC) made of beryllium copper and is in the form of a cylindrical microbellow. Preliminary loop tests in the absence of an inhibitor resulted in a localized attack within 3 months in the FTC after exposure to circulating city water. In inhibited circulating water with 500 ppm of benzotriazole(BTA), however, maximum penetration in the FTC was estimated to be less than 0.01 micrometer after 1 month. The surface color of the FTC remained off-bright and there was no sign of corrosion. XPS analysis was conducted on FTC's used for 3 months and 2 years in a water-cooled computer. Elements of Cu, O, C and N were detected on the inner surfaces of both FTC samples. These elements were attributed to aromatic carbons, heterocyclic nitrogen in BTA and copper oxides on the beryllium copper surface. The XPS data indicate the existence of a copper-benzotriazole complex (Cu-BTA) film formed on copper oxide (Cu_2O) on the surface of FTC in circulating cooling water containing BTA. It was concluded that benzotriazole can be successfully applied as a corrosion inhibitor to prevent a localized attack in thin-walled (about 40 micrometers in thickness) FTCs in a water cooling system. (English)

Inhibition of Copper Corrosion in Domestic Water Using Ca, Mg and Na-Salts of Phytic Acid

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

Corrosion Science, **37**, [1], 55-65 (1995)

Phytic acid has been proposed as an inhibitor of copper corrosion in potable waters. This paper concerned with the inhibiting action of the Ca, Mg and Na- salt derivatives of phytic acid which have, to date, been little studied. A synthetic domestic water (SDW) (pH=6.8) containing 36.6 mg/l HCO_3^-, 42.6 mg/l Cl^-, 76.8 mg/l SO_4^{2-} and 100 mg/l NaClO was prepared and the corrosion behaviour of copper in solutions containing different levels of the three salts alone was evaluated by potentiodynamic and potentiostatic techniques at 30 and 65 ℃. Uniform corrosion was found to occur in the SDW and this was inhibited by the Ca and Mg-salts. These salts have a limited solubility and the relative inhibition efficiency of Ca and Mg-phytate saturated solutions was caluculated at 12.3 % and 22.3 % respectively. The Na-phytate was completely soluble and promoted the formation of a passive film. At the 10 mM level the relative inhibition efficiency was 99.6 %. Additions of Na-phytate caused marked increase in pH of the SDW but this could be countered by dosing with acid without sacrificing markedly its inhibiting effect. Pitting corrosion could be induced below a certain level of the Na-salt. At higher concentrations pitting corrosion was prevented and there was no visible evidence of corrosion products on the Cu electrode. Surface analysis indicated the formation of a Cu-phytate film on top of the copper oxide film. (English)

A Study of Corrosion Prevention of Thin-Walled Copper Alloy Bellows for a Water-Cooled Super Computer with Corrosion Inhibitors

T. Notoya, H. Yamamoto, K. Katsuyama and M. Miyo

Journal of the Japan Copper and Brass Research Association,

34, 127-132 (1995)

A new water cooling system for high-speed and high-density LSIs has been developed to meet the demand for rapid increases in super computer performance. The cooling system consists of a cooling header and a flexible thermal conductor (FTC) made of beryllium copper and is in the form of a cylindrical microbellow. Prelimiary loop tests in the absence of an inhibitor resulted in a localized attack similar to "ant's nest corrosion" within 3 months in the FTC after exposure to circulating city water. In inhibited circulating water with 500 mg/l of benzotriazole or its derivative inhibitor, however, maximum penetration in the FTC was estimated to be less than 0.01 micrometer after 1 month. The surface color of the FTC remained off-bright and there was no sign of corrosion. XPS analysis was conducted on FTCs used for 3 months and 2 years in a water-cooled computer. Elements of Cu, O, C and N were detected on the inner surfaces of both FTC samples. These elements were attributed to aromatic carbons, heterocyclic nitrogen in benzotriazole and Cu_2O on the beryllium copper surface. The XPS data indicate the existence of a copper-benzotriazole complex film formed on copper oxide on the surface of FTC in circulating cooling water containing benzotriazole. It was concluded that the inhibitor can be successfully applied as a corrosion inhibitor to prevent a localized attack in very thin-walled FTCs in a water cooling system. (Japanese)

Investigation of High-Temperature Molten Salts Predominantly Composed of Chloride for Aluminum-Electrorefining

Mikito Ueda, Shoichi Konda, Takeshi Sasaki
and Tatsuo Ishikawa

Denki Kagaku, **63**, 664-668 (1995)

For electrorefining of Al from aluminum scraps by using a bipolar electrode system, characteristics of $BaCl_2$-NaCl, less-corrosive melts to cell materials than fluoride melts, were investigated. Measuring the densities as a function of their compositions showed that melts containing $BaCl_2$ over 50 mol% had higher densities than that of liquid Al(2.35g • cm^{-3} at 800℃) and were applicable as a base melt to the bipolar electrode system. Next, methods for adding aluminum components into the $BaCl_2$-NaCl were examined in terms of their solubilities and stabilities. Only by feeding double salts of 40~43mol%AlF_3-NaF, a significant concentration of aluminum components was attained in the $BaCl_2$-NaCl. The proposed melt for the bipolar electrode system is as follows : 10mol% AlF_3 -15mol%NaF-41mol%$BaCl_2$-34mol%NaCl. The low corrosivity of this melt against quartz materials has also been confirmed. (Japanese)

Analysis of Solidification Path of Fe-Cr-Ni Ternary Alloy

K. Ohsasa, S. Nakaue, M. Kudoh and T. Narita

ISIJ International, **35**, 629-636 (1995)

The solidification path of an Fe-Cr-Ni ternary alloy was calculated numerically on the basis of thermodynamic analysis. In order to evaluate the effect of back diffusion in the solid, three models are used for the analysis. That is, 1) a equilibrium model with perfect diffusion in the solid, 2) the Scheil model with no diffusion, 3) a limited back diffusion model. and obtained results were compared. In the calculations, the equilibrium tie line at the solid-liquid interface, which varies depending on both temperature and composition, was determined for each step of numerical computation. The solidification path with back diffusion was calculated by a new technique combining thermodynamic calculation and diffusion analysis. In this model, δ - γ transformation. which occurs during solidification of the Fe-Cr-Ni ternary system, was dealt with under the assumption that the transformation is diffusion controlled. The relationship between temperature and the fraction solid of the ternary alloy for different cooling rates obtained from the limited back diffusion model was located between those obtained from the equilibrium and Scheil models, demonstrating the validity of the analysis. (English)

Oxidation of Silicides and Its Subjects

Kazuya Kurokawa

Text of the 22nd Corrosion Seminar (JSCE), 63-82 (1995)

One of the inherent problems in designing structural materials for high-temperature use is their reaction with an oxidizing environment. Therefore, many works have focused on developing materials with both structural integrity and oxidation resistance. Molybdenum disilicide ($MoSi_2$) has a high melting point (2303 K) and exhibits a brittle-to-ductile transition at about 1273 K. In addition, because of its outstanding oxidation resistance at high temperatures by the formation of a highly protective SiO_2 layer, it has many attractive applications in high-temperature oxidizing environments. In this text, the oxidation resistance and the barrier to extensive application of $MoSi_2$-based ultra-high temperature materials were described. (Japanese)

Oxidation Behavior of $MoSi_2$-WSi_2 Solid Solutions

Kazuya Kurokawa and Hiroki Matsuoka

Report of the 123rd Committee on Heat-Resisting Metals and
Alloys in Japan Society for the Promotion of Science,
36, [1], 83-90 (1995)

From a thermodynamical consideration, $MoSi_2$ and WSi_2 are expected to easy to form a protective SiO_2 layer in comparison with other refractory-metal disilicides. It was in fact confirmed that the disilicides had outstanding oxidation resistance at high temperatures such as 1473 and 1773 K as a result of the selective oxidation of Si. Such passive oxidation behavior was identical also in all $MoSi_2$-WSi_2 solid solutions. However, at lower temperatures, especially at a medium temperature like 1073 K, active oxidation which was based on the simultaneous oxidation of W and Si took place in the 50%WSi_2 specimen. It was thermodynamically and experimentally confirmed that the preoxidation at higher temperatures was effective for the prevention of active oxidation. (Japanese)

Oxidation of Ultra-High Temperature Materials

Kazuya Kurokawa

Shinsozai, **6**, 19-23 (1995)

The factors which contorol the formation of a protective oxide layer on structural materials at high temperatures were discussed under thermodynamical and kinetic considerations. In particular, the conditions for selective oxidation were discussed. SiO_2-formers such as $MoSi_2$, SiC, and Si_3N_4 have extremely excellent oxidation resistance, hence it may be concluded that those materials are the most promising ultra-high temperature materials. (Japanese)

Effect of Manganese on the Initial Oxidation of Type 430 Stainless Steels at 1273 K

Isao Saeki, Hidetaka Konno, and Ryusaburo Furuichi

Material Science Forum, **192-194**, 535-542 (1995)

Type 430 stainless steels having different manganese content of 0.09-0.9 mass% were oxidized at 1273 K in a 0.165 atm O_2-balance N_2 atmosphere and the oxide properties and oxidation behavior were examined by SEM, XPS, XRD and electrochemical impedance spectroscopy (EIS). Just after the specimen temperature arrived at 1273 K (it took 20 s and referred to as t_{ox} =0 s), a number of fine particles were scattered on the surface of all alloys, though there may be formed very thin oxide film. The oxide growth and film formation was observed from t_{ox} =15 s and the surface of t_{ox} =15-60 s was relatively flat on 0.9 Mn alloy compared with 0.09 Mn alloy. Within t_{ox} =180 s, however, uniform oxide film was not formed and oxidation rates did not follow any kinetics with all alloys. Apparent thickness of the oxide films was thicker on 0.09 Mn alloy than on 0.9 Mn alloy. The oxide formed on 0.09 alloy consisted of a corundum type film with iron ion rich outerpart and chromium ion rich innerpart at t_{ox} =0 s, whereas the structure reversed at t_{ox} =60 s. With alloys having Mn$\geqq$0.38 mass%, however, both corundum and spinel type oxides were formed at t_{ox} =60 s. There were different responses in electrochemical impedance spectra from the oxide films between 0.09 Mn and 0.9 Mn alloys. They reflected the differences in composition and morphology of the oxide and EIS was found to be a useful technique to characterize the oxide films formed by high temperature oxidation. (English)

XPS Characterization of Oxide Films Formed on Fe-Cr Alloys during the Initial Period at 1273 K

Hidetaka Konno, Isao Saeki, and Ryusaburo Furuichi

Zairyo-to-Kankyo (Corrosion Engineering), **44**, 30-36 (1995)

The Fe-(10-30)Cr alloys were oxidized for 60 s at 1273 K in 0.05 atm H_2O-air with an infrared radiation furnace. Formed oxide films were characterized mainly by XPS : XRD and ellipsometric measurements were also done. As rolled alloys were a single-phase except for a 10Cr alloy and the average grain size was 52±8mm(±1s). They were wet emery polished down to 1000, mirror finished with diamond slurry, and left in a silica gel desiccator for one day before use. The pretreated specimens were covered with $(Fe_{1-y}Cr_y)OOH$ film of about 2 nm thick which contained very small amount of silicate, manganese and sulfur species : y increased proportionally with Cr content in alloy but less than that in alloys. The oxide scale formed on 10Cr alloy was thick and showed spalling : structure and composition of the scale are similar to those formed on type 430 stainless steel by breakaway oxidation. Thin oxide film of $(Fe_{1-y}Cr_y)_2O_3$ was formed on (16-30)Cr alloys, x being less than 0.03 for 16Cr alloy and decreased with Cr content in alloy. Bound water was detected only in the outer-most part. The thickness was estimated to be more than 100 nm and increased with Cr content in alloy. It might be explained by the formation of coarse and uneven films due to the short period. (Japanese)

High Temperature Oxidation Behavior of Plasma Sprayed MCrAlY Coatings

H. Taumi, Y. Harada, M. Nakamori and T. Narita

Proceedings of ITSC '95, Kobe, 453-458 (1995)

Three MCrAlY (M = Co, Ni and CoNi) coatings were prepared by Air- and Vacuum- Plasma Spraying methods (APS and VPS) in order to measure such properties as density, microstructure, thermal expansion coefficient, and high-temperature oxidation properties. The as-sprayed APS samples showed an abnormal temperature dependence on thermal expansion coefficients due to changes in microstructures accompanied by change in density, and with repeated measurements they tended to obey a normal temperature dependence.

Oxidation rates of the VPS NiCrAlY were much higher than those of the VPS CoCrAlY and CoNiCrAlY, and the former had an α -Al_2O_3 Scale and an Al depleted subsurface layer thicker than those formed on the latter two. Further, in the case of the VPS NiCrAlY an yttrium-rich phase appeared within the reaction zone. (English)

Localized Surface Treatment of Metals and Ceramics with Laser Irradiation

Hideaki Takahashi, Katsutoshi Nukui, and Jyun Wakabayashi

Materia Jpn., **34**, 1276-1283 (1995)

Localized surface treatment of metals and ceramics with laser irradiation has been reviewed and recent work at our laboratory on the localized anodizing of aluminum and Cu-plating on Aluminum with pulse YAG-laser has been introduced. In the review, laser-enhanced electroplating and electroless plating, and etching was described to apply them for surface patterning of metals and ceramics. Porous anodic oxide films could be formed at a selected area on aluminum with pulse YAG-laser and dyed only the localized area successfully. A fine pattern on aluminum was made with Cu-plating line with 50 μm width by pulse YAG-laser. (Japanese)

Film Breakdown and Pit Formation during Cathodic Polarization of Aluminum Covered with Anodic Oxide Films : Effect of Film Preparation and Structure

Hideaki Takahashi, Kazutoshi Fujiwara, and Masahiro Seo

Material Sci. Forum, **185-188**, 1001-1010 (1995)

Cathodic polarization behavior of aluminum covered with different types of barrier anodic oxide film has been investigated in a neutral borate solution to examine how the structure of the film affects the film breakdown and pit formation during the cathodic polarization.

Highly pure aluminum specimens were anodized in a neutral borate solution after a) electropolishing (BS-specimen), b) surface-roughening (BR-specimen), c) heat treatment (TA-specimen), or d) hydrothermal treatment (HA-specimen), and then polarized cathodically by scanning the potential at 2.9 V／s in the neutral borate solution.

Cathodic polarization curves for all specimens showed a very small value of cathodic current, i_c, at potentials higher than -2 - -4V, and beyond these i_c increased appreciably with lowering E_c. The i_c vs. E_c curve at the low potential region shifted in the anodic direction in the order of BS-< BR-< HA-< TA-specimens. The scanning electron microscopy showed the evidence of pits after the cathodic polarization, and the number of pits, N_p, depended strongly on the kind of preexisting oxide film. The value of N_p was between 10^3 and10^6／㎠, increasing in the order of BS-< BR-< HA-< TA-specimens. The ratio of corrosion rate of the metal substrate to electrochemical reduction rate was between 0.02 - 0.8, increasing in the order of BS-< HA-< BR-< TA-specimens.

The cathodic polarization behaivor is discussed in terms of the film breakdown initiating at the site of imperfections in the oxide films. (English)

Local Anodizing of Aluminum in a Sulfuric Acid Solution with Laser Irradiation

Hideaki Takahashi, Katsutoshi Nukui, Masahiro Seo
Yutaka Matsumi, and Masahiro Kawasaki

Proc. 7th Intern. Symp. on Oxide Films on Metals and Alloys, 50-61, (1995)

Aluminum specimens covered with several types of insulating oxide film were anodized potentiostatically in a sulfuric acid solution after irradiation with a pulse YAG-laser, and the properties of the anodic oxide films were examined by FTIR, SEM, and dyeing experiments.

Porous type oxide films with pore-branching were found to be formed only at the laser-irradiated area during the subsequent anodizing. The growth rate of the anodic oxide films after laser irradiation was slower than that for electropolished specimens without laser irradiation, and did not depend on the type and thickness of the insulating oxide films.

Film formation mechanisms after laser irradiation are discussed in terms of ablation and formation of the oxide film by laser and inhibition of ion transport by the formed oxide during anodizing. (English)

Surface Morphology and Electroluminescence of Porous Silicon Layer Prepared on P-Type Silicon with Electrochemical Etching in HF Aqueous Solutions

K. Shigyo, M. Seo, K. Azumi, H. Takahashi,
M. Al-Odan, and W. H. Smyrl

Electrochemical Society Proceedings, **95-8**, 3-14 (1995)

Porous silicon layer (PSL) was prepared on single crystal p-type Si (100) wafers with electrochemical etching under a galvanostatic condition in HF aqueous solutions to explore the optimum preparation condition of PSL for good adherence to the substrate and for good reproducibility of visible luminescence with high intensity. The surface morphology of PSL was observed with various microscopic techniques (SEM, TEM, AFM, and CLSM) and electroluminescence (EL) emitted from PSL during anodic oxidation in KNO_3 aqueous solution in addition to photoluminescence (PL) was measured to understand the luminescence mechanism.

Both EL and PL intensities depended sensitively on HF concentration and specific resistivity of the substrate. The adherence of PSL with the substrate was evaluated from the SEM images of cross section of PSL. The optimum preparation condition of PSL was finally obtained when the specimen with specific resistivity of r = 10 ohm cm was electrochemically etched under a galvanostatic condition of i = 1 mA cm^{-2} for 250 min. The TEM image of PSL with a high magnification (5×10^5) has suggested that the quantum confinement effect is operative in the visible luminescence. (English)

Joining and Interfacial Reaction in a $MoSi_2$／Ti／Graphite System by Spark Plasma Sintering

Kazuya Kurokawa and Tetsushi Horibe

J. Institute of Appl. Plasma Sci., **3**, 7-12 (1995)

As a basic research on the improvement of oxidation resistance of C／C composite, joining of $MoSi_2$ to graphite with a titanium foil has been tried by using a spark plasma sintering equipment (SPS). The interfacial reactions in a $MoSi_2$／Ti／graphite system were discussed by considering the phase diagrams. In the system, the formation of a SiC layer was perfectly suppressed and TiC and Mo_5Si_3 layers were formed. Moreover, the flexual strength of the joined specimens was measured and the maximum strength was achieved in joining at 1873 K. (Japanese)

Migration Behavior of Sodium Ions in Compacted Sodium Montmorillonite

T. Kozaki, A. Fujishima, S.Sato, H. Ohashi

Bull. Fac. Eng. Hokkaido Univ., **175**, 87-95 (1995)

Apparent self-diffusion coefficients of sodium ions in compacted sodium montmorillonite were determined so as to obtain basic data for safety assessments of geological disposal of high level radioactive wastes. The self-diffusion coefficients of sodium ions obtained were in the range from 1.2×10^{-11} to 1.2×10^{-10} m^2 s^{-1} under various conditions at temperatures from 278K to 323K for the compacted montmorillonite of dry density from 1.0 to 1.8×10^3 kg m^{-3}.

Retardation factors and distributi coefficients (S／L ratio) were calculated from the diffusion coefficients obtained at 303K. The retardation factors and the distribution coefficients were in the range from 1.5 to 2.8 and from 1.1×10^{-3} to 1.0×10^{-4} m^3 kg^{-1}, respectively. The distribution coefficients decreases with increasing dry density of montmorillonite. The dry density dependence of the distribution coefficients of sodium ions was compared with that reported for cesium and strontium ions. The dry density dependence of sodium ions was almost same as strontium ions, but different from cesium ions. This suggests the relationship between distribution coefficients and radii of hydrated cations.

Activation energy was obtained from the temperature dependence of the diffusion coefficients of sodium ions. It was found that the activation energy increases with increasing dry density of montmorillonite. This can be attributed to the change in diffusion path for sodium ions in the compacted bentonite caused by the change in the dry density of montmorillonite. (Japanese)

Surface Reactions on Palladium Hydride in Vacuum, Air and Water Studied in Situ with Mass Spectrometry

L. Grasjo, G. Hultquist, K. L. Tan, and M. Seo

Applied Surface Science, **89**, 21-34 (1995)

The release of hydrogen from palladium hydride was studied in different environments, vacuum, open air with ~40 % relative humidity, air with varying relative humidity contained in a virtually closed volume, and from a sample immersed in liquid water. The release was followed in situ using mass spectrometry in vacuum and in limited volume, and by measuring the weight change of the sample in open air. Based on the experimental results we conclude that in addition to the release in the form of molecular hydrogen, the main route in air and liquid water in contact with air, is reaction with oxygen. Further it was found that water catalyzed the reaction between hydrogen and oxygen and thereby increased the release rate of hydrogen by a factor $>$ 100. (English)

Hydrogen Absorption and Hydride Formation in Ti during Cathodic Electrolysis

T. Mizuno and M. Enyo

Denki Kagaku, **63**, [8], 719-725 (1995)

Relationships between electrochemical kinetics of hydrogen absorption by electrolysis and hydrogen concentration profiles of Ti were investigated by a nuclear chemical and a chemical technique. Hydrogen atoms inter, diffuse and form a hydride layer in the metal by cathodic polarization. In the process hydrogen atoms interact very intensively with each others. Hydrogen concentration profiles in the hydride layer were dependent on the condition of cathodic electrolysis and pre-treatment of metal. A anomalouse 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. (Japanese)

Formation of ^{197}Pt Radioisotopes in Solid State Electrolyte Treated by High Temperature Electrolysis in D_2 Gas

T. Mizuno, K. Inoda, T. Akimoto, K. Azumi, M. Kitaichi,
K. Kurokawa, T. Ohmori and M. Enyo

Infinite Energy, **1**, [4], 9-11 (1995)

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 in all samples charged with an alternating current with voltages ranging from 5V a d 45V, at temperatures ranging from 400 to 700℃. 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. (English)

Effect of pH on the Dissolution Rate of Magnetite in Solutions Containing Chelating Agents

Shinichi Takasaki, Kazuyoshi Ogura, Hiroki Tamura,
and Masaichi Nagayama

Zairyo-to-Kankyo (Corrosion Engineering),
44, 86-93 (1995)

The dissolution behavior of magnetite powder (as received) and pellet (prepared by sintering) in solutions containing EDTA or citrate was studied at different pHs (0.3～9) and temperatures (30～95℃). The concentration of dissolved Fe increased with time, and is highest at pH 2.4 with EDTA and at pH 3.7 with citrate. A rate equation of dissolution was derived from a consideration that the dissolution reactions consist of the following two coupled processes : (1) the transfer of Fe ions from solid to aqueous phase by reaction with chelating agents and (2) the transfer of lattice O^{2-} ions by reaction with H^+ to form H_2O. The resulting rate equation in solutions with EDTA (H_4Y) is

$$d[Fe]/dt=k'k''[H^+]^{8/3}\alpha_4([Y]_T-[FeY])/(k'[FeY]+k''[H^+]^{8/3})$$

where k' and k" are the rate constants for the processes (1) and (2), α_4 is the ionization fraction of Y^{4-}, and $[Y]_T$ is the total concentration of EDTA. The amount of dissolved Fe vs. pH peaks at a specific pH, which can be explained by the rate equation noted above. (Japanese)

Reductive and Chemical Dissolution of Magnetite in EDTA Solutions under Cathodic Polarization

Shinichi Takasaki, Kazuyoshi Ogura, Hiroki Tamura, and
Masaichi Nagayama

Zairyo-to-Kankyo (Corrosion Engineering),
44, 557-565 (1995)

Chelating agents are being used to remove radioactive contaminants in the corrosion products of cooling systems of nuclear poser plants. To elucidate the reaction mechanism the dissolution rate of sintered magnetite pellets in solutions with and without EDTA was measured as a function of potential (0.6 ～ −1.2 V vs. saturated Ag／AgCl electrode) and pH (1.1～4.6) at 80℃. It was found that two kinds of reaction can occur : (a) reductive dissolution and (b) chemical dissolution due to chelate formation. Without EDTA only reductive dissolution occurs in the potential range 0.6～ −1.2 V. At pH 1.1 the dissolution rate shows a maximum at 0 V, the distillation peak shifts to more negative values, and the peak height decreases as pH is increased. In the presence of EDTA only reductive dissolution occurs at pH 1.1, but at pH 2.5 chemical dissolution proceeds as well as the reductive dissolution, showing a maximum dissolution rate at 0 V. These results were explained by (1) the transfer of Fe ions from solid to aqueous phase to form aqua ions or EDTA chelates and (2) the transfer of lattice OH^- or O^{2-} ions by reaction with H^+ ions to form H_2O. (Japanese)

Kinetic Modeling of Incorporation of Lithium Ions into a Spinel Type Manganese Oxide, a Template Ion Exchanger

Akira Uchibo, Hiroki Tamura, and Ryusaburo Furuichi

Bunseki Kagaku, **44**, 449-455 (1995)

A "lithium ion memory" template ion exchanger, a spinel type manganese oxide ($\square Mn_2O_4$) with vacancies ($\square$), has shown promise for preliminary concentration of trace lithium ions in natural environments. This oxide was prepared by topotactic extraction of lithium with nitric acid from a spinel type $LiMn_2O_4$, which was obtained by a solid-phase reaction between Li_2CO_3 and Mn_2O_3 at 850℃. The formed spinel type manganese oxide was characterized by XRD, SEM, EDX, AAS, and BET surface area measurements. The amount of lithium ions incorporated into the oxide was measured by AAS of lithium ions in solution and by an analysis of hydroxide ions in solution with pH measurements or titration according to the stoichiometry shown below. The lithium ion uptake reaction was maintained for more than one month, and the stoichiometry was confirmed as

$\square Mn(IV)_2O_4 + Li^+ + OH^- \rightarrow LiMn(III)Mn(IV)O_4 + 1/4O_2 + 1/2H_2O$

The average velocity of Li^+ incorporation for 1 day, V, increases with the lithium ion concentration tending towards limiting values, while it increases exponentially with pH.

The following kinetic model is proposed :

$$(1)\ {=}Mn(IV) + OH^- + \square \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {=}Mn(III) + \square^* + 1/4O_2 + 1/2H_2O$$

$$(2)\ \square^* + Li^+ \xrightarrow{k_2} {=}Li(I)$$

where k_1, k_{-1}, and k_2 are the rate constants of respective elementary reactions. This assumes that the oxidation of a hydroxide ion by the lattice Mn(IV) ion excites a vacancy with a slight backward reaction and that the excited vacancy takes up a lithium ion. The rate equation for V obtained by applying the steady state approximation to the excited vacancy explained the observed results well. (Japanese)

Modeling of Ion Exchange Properties of Carboxyl Sites Distributed in Resin Pores

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A model to evaluate the properties of carboxyl groups of weak acid cation-exchange resins was developed by assuming that the resins have sites with different reactivities (polyfunctionality) and that the ion exchange at a site is suppressed with the progress of the reaction due to repulsive lateral interactions between adsorbed ions. The model was applied to the alkali-metal ion/proton exchange behavior observed by titration with Amberlite IRC-50, a macroreticular type ion-exchange resin. It was found that there are two types of sites with similar ion-exchange intensities but different lateral interactions. The different reactivities of carboxyl sites were ascribed to the micro- and macropore environments in the resin networks. (English)