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Laboratory names changed due to the change of the organization of the Faculty of Engineering, Hokkaido University.

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CORROSION ENGINEERING LABORATORY

Prof. Dr. T. Ishikawa, Assoc. Prof. T. Sasaki,
Lecturer Dr. T. Notoya, and Tech. Staff S. Konda

Students

M. Ueda, S. Hara, S. Kobayashi, Y. Kondo, T. Itoh,
H. Nakamura, N. Ohya, T. Abe, J. Itoh,
H. Nakagawa, and T. Tada

Professor Ishikawa attended The 9th International Symposium on Molten Salts in San Francisco, California, in May and assoc. Prof. Sasaki was presented at The 185th Meeting of Electrochemical Society in May in the same place.

Professor Ishikawa and Mr. Ueda also attended The 5th China-Japan Bilateral Conference on Molten Salt Chemistry and Technology in Kunming, China, in September.

Dr. Notoya visited Dr. Schweinsberg, Queensland University of Technology, Brisbane, Australia in January. Dr. Notoya, Dr. Schweinsberg and Professor Geesey, Montana State University, have been planning a joint research of "Prevention of Blue Water Problems in Domestic Water" sponsored by International Copper Association.

Dr. Notoya attended the International Symposium on Localized Dissolution/Corrosion, TMS/ASM Annual Meeting at Rosemont, Illinois, U.S.A. in October.

Professor D. A. Scherson, Dept. of Chemistry, Case Western Reserve University, Ohio, U.S.A., visited this laboratory on January 18–20 and discussed the current studies on *in situ* spectroelectrochemistry and gave a lecture on the theme.

Researches in progress are as follows.

(1) To save energy in producing pure aluminum from aluminum scraps, an electrochemical cycle system has been developed. A three-phase electrolysis system for an electrorefining of aluminum scraps, one component step of the system, was proposed and its

electrochemical characteristics is under study. The characteristics of active areas for reduction of chlorine in an aluminum-chlorine fuel cell, other component step of the system, is also under investigation.

(2) Laboratory-scale tests for electrowinning of liquid aluminum and its titanium alloys by using bipolar electrode cells are being carried out in alkali and alkaline earth chloride molten salts containing $AlCl_3$ and $TiCl_4$ in the temperature range from 700 to 800°C.

(3) The morphology and the electrochemical characteristics are being studied in co-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 and spectroscopic investigations of copper and tin-lead alloys are in progress.

(6) Surface layers initially produced on copper and iron in atmospheric corrosion environments are being investigated by *in situ* spectroscopic techniques.

(7) The performance of inhibitive action of benzotriazole derivatives are being explored for copper and copper alloys by using immersion tests and electrochemical techniques. The mechanisms of a localized corrosion in copper tubes are also studied under simulated conditions.

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

Presentations

Effect of Aging Temperature on Behavior of Passive States of SUS 430 Stainless Steel; T. Matsuhashi, T. Sasaki and T. Ishikawa: The 1994 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Corros. Eng. Soc., and Surf. Finish. Soc., Sapporo, Jan., 1994.

In situ IR Spectroscopy of Corrosion Products of Fe and Cu; M.

Nakata, T. Itoh, T. Sasaki and T. Ishikawa: *ibid.*

Solubility and Behavior of Aluminum Halides in $BaCl_2$-NaCl Molten Salts; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: The Winter Meeting of Hokkaido Section of Jpn. Inst. Metal, Sapporo, Jan., 1994.

In situ IR Spectroscopy of Surface Layers Produced at Initial Stages of Atmospheric Corrosion; M. Nakata, T. Itoh, T. Sasaki and T. Ishikawa: The 89th Annual Meeting of Surface Finishing Soc. Jpn., Tokyo, March, 1994.

In situ IR-RAS Observation of Aromatic Thiols Adsorbed on Gold Electrodes; T. Sasaki and T. Ishikawa: *ibid.*

Effect of Heat Treatment on "Ant's Nest Corrosion" in Copper Tubes; T. Notoya, T. Ishikawa, T. Hamamoto and T. Tsuji: The 66th Spring Meeting of Jpn. Chem. Soc., Tokyo, Mar., 1994.

Method for Introducing AlF_3 to a $BaCl_2$-NaCl Molten Salt System: The 61st Meeting of Electrochem. Soc. Jpn., Sendai, Apr., 1994.

In situ IR-RAS Investigation of Electrochemical Reaction of Aromatic Thiols Adsorbed on Gold Electrodes; T. Sasaki, S. Hara and T. Ishikawa: *ibid.*

Dissolved States of Divalent Metal Chlorides in $AlCl_3$-NaCl Melts; T. Ishikawa, T. Sasaki, S. Konda and M. Noguchi: The 9th International Symposium on Molten Salts, San Francisco, May, 1994.

Band Shifts of Infrared Spectra of Aromatic Thiols Adsorbed on Gold Polycrystalline Electrodes with Potential; T. Sasaki and T. Ishikawa: The 185th Electrochem. Soc. Meeting, San Francisco, May, 1994.

Initial Stage of Atmospheric Corrosion of Fe and Cu as Studied by *in situ* Infrared Reflection Absorption Spectroscopy; T. Sasaki, M. Nakata and T. Ishikawa: *ibid.*

Initial Stages of Corrosion of Copper in Atmospheric Environment Containing SO_2; T. Itoh, T. Sasaki and T. Ishikawa: The Summer Meeting of Hokkaido Section of Jpn. Inst. Metal, Sapporo, June, 1994.

Reaction between Liquid Aluminum and Gaseous Titanium Chloride; Y. Kondo, T. Kumagai, S. Konda, T. Sasaki, T. Chiba and T. Ishikawa: *ibid.*

Copper Corrosion Inhibition with Ca-phytate, Mg-phytate in Tap Water; T. Notoya, V. Otieno-Alego and D. P. Schweinsberg: 94 Spring Meeting of Jpn. Soc. of Corro. Eng., Tokyo, July, 1994.

Electrochemical Formation of Cu-benzotriazole Films on Copper Electrode and Its Inhibition Mechanisms; T. Notoya: The 14th Meeting of Jpn. Rust Prevention Association, Tokyo, July, 1994.

Surface Protection on Copper Alloy Bellows for Water-Cooled Super Computers; T. Notoya, H. Yamamoto and M. Miyo: The 1994 Summer Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Muroran, July, 1994.

In situ IR-RAS Spectroscopic Studies of Atmospheric Corrosion Layers Initially Produced on Cu and Fe; T. Itoh, M. Nakata, T. Sasaki and T. Ishikawa: The 94 Fall Meeting of Electrochem. Soc. Jpn., Yokohama, Sep., 1994.

In situ IR Studies of Atmospheric Corrosion; T. Sasaki and T. Ishikawa: *ibid.*

On Active Places for Reduction of Chlorine in an Al-Cl_2 Fuel Cell; S. Konda, T. Sasaki and T. Ishikawa: *ibid.*

Fundamental Studies on High-Temperature Molten Salts for Electrorefining of Liquid Aluminum; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: The 5th China-Japan Bilateral Conference on Molten Salt Chemistry and Technology, Kunming, China, Sep., 1994.

The Effect of Phytic Acid Derivatives on the Corrosion Behavior of Copper in Simulated City Water; T. Notoya, V. Otieno-Alego and D. P. Schweinsberg: The International Symposium on Localized Dissolution/Corrosion 1994 Fall TMS/ASM Meeting, Rosemont, U.S.A., Oct., 1994.

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: *ibid.*

Initial Corrosion Layers Produced in Atmospheric Environment; T. Itoh, T. Sasaki and T. Ishikawa: The 90th Meeting of Surface Finishing Soc. Jpn., Sapporo, Oct., 1994.

Characteristics of Reaction between Liquid Aluminum and Gaseous Titanium Tetrachloride in molten Salts; Y. Kondo, T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The 26th Meeting of Molten Salt Chemistry, Sapporo, Nov., 1994.

Characteristics of Deposition Reaction of Al in $BaCl_2$-NaCl Salts Containing AlF_3; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa *ibid.*

Corrosion Protection of Thin-Walled Beryllium Copper Bellows for Water-cooled Super Computer with Benzotriazole; T. Notoya, H. Yamamoto, K. Katsuyama and M. Miyo: The 34th Meeting of Jpn. Copper and Brass Research Association, Tokyo, Nov., 1994.

In situ Investigation of Layers Initially Produced in Atmospheric Corrosion Environments; T. Sasaki, T. Itoh and T. Ishikawa: The 14th Meeting on Spectroscopic Investigation of Adsorbed Molecules, Tatsuguchi-cho, Nov., 1994.

MATERIALS CHARACTERIZATION CHEMISTRY LABORATORY

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

Students

A. Furusaki, A. Uchibo, R. Hata, T. Abe, K. Utaka,
N. Ohkushi, K. Kuribayashi, T. Miyai, M. Itoh,
T. Saito, and K. Mita

Our laboratory name was changed from Analytical Chemistry to the above due to the change of the organization of the Faculty of Engineering, Hokkaido University, and Dr. Konno moved to a newly established laboratory as an Assoc. Prof. Our research activities are still in characterization and evaluation of surface properties, surface reactions, surface compositions, and surface morphologies of materials.

Prof. Furuichi and Furusaki joined the International and the 3rd Sino-Japanese Joint Symposium on Thermal Measurements '94 held at Xi'an, China, in June. Prof. Furuichi and Dr. Tamura were on the organizing committee of the International Trace Analysis Symposium '94 held at Hakodate and Sapporo in August, and made presentations at the symposium. Saeki joined International Symposium on Electrochemical Method in Corrosion Research '94 held at Sesimbra, Portugal, in September.

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. This oxide was prepared and modeling of the kinetics of lithium incorporation is being made by applying the "steady-state approximation" to the excited state of vacancies.

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

The behavior of fine metal oxide particle/water systems are important in industry and natural environments. The acid-base, charge, and ion adsorption characteristics of metal oxide surfaces accompanied by ion exchange reactions are studied, and modeling of ion exchange equilibria are made with the Frumkin isotherm for characterization purposes. It is found that the ion exchange ability of metal oxides can be explained with the electronegativity of oxide lattice metal ions and the adsorption affinity of ions with the tendency of ions to form hydroxo complexes in homogeneous solutions.

(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 studied as a function of pH, and it was found that the dissolution rate shows a maximum at a certain pH. Kinetic modeling was made by assuming that the dissolution reaction involves two coupled processes: (a) the transfer of Fe ions by reaction with EDTA to form chelates; and (b) the transfer of lattice oxide ions by reaction with H^+ ions to become H_2O. The model reproduces the kinetic behavior of dissolution well.

(4) Formation of perovskite structure La(III)-Cr(III)-Mn(III) oxide films by spray pyrolysis

A novel synthesis method of $(La_{1-x}A_x)(Cr_{1-y}B_y)O_3$[A = Ca(II) or Sr(II), B = Mn, Co and so on] was developed to form thin oxide films on ceramics and metals. The method utilized ultrasonic spraying and pyrolysis. The formation rate of films was found to depend on spraying time and substrate temperature. The deposited precursor films were converted to perovskite oxides by the pyrolysis at 800°C for 15 min in nitrogen. Further investigations on the pyrolysis mechanism were carried out by various types of thermal analysis.

(5) Electrochemical formation of mixed oxide films on metals

Cathodic deposition method to form gel-like thin films (around 1 μm in thickness) on metals was developed. Here, cathodic reduction of nitrate ions was used to control the surface pH. Hydroxide films of Al(III), Ce(III, IV), Y(III), Zr(III, IV) and mixed hydroxide films were formed on metals. After drying at 350°C, the films showed good performance as protective oxide coatings for stainless steels under oxidizing atmospheres at elevated temperatures.

(6) Formation of composite anodic oxide film on aluminium

A novel anodizing process for aluminum was developed to form porous oxide films which contain heavey metal ions. The process consists of two steps: first the formation of a metal-oxyhydroxide film on aluminium and second anodizing in acid solutions. The outer part of the anodic oxide films contains metal ions such as molybdenum, chromium, and other heavy metal ions. It was found that films formed by this process have higher hardness and better corrosion resistance in chloride media than the films formed by conventional anodizing under the same conditions.

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

TiO_2 is 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. Much works have been made to improve the properties of TiO_2 elctrodes. In this study, composite oxides of Ti and M (M=W, Ta, Mo, Ni, 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 and Ta show higher anodic photocurrents than pure TiO_2.

(8) Initial stage of the high temperature oxidation of Fe–Cr alloys

There are many works on the high temperature oxidation of Fe–Cr alloys. Many of them are 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 information about the oxidation at much longer time and about operation of stainless steel production, especially descaling and annealing processes. In this work, thin films grown on Fe–Cr and Fe–Cr–Ni alloys oxidized in 1 atm of oxidizing gas for 0 to 1800 s at 1073–1273 K were analyzed with several methods (TLXRD, XPS, AES-SAM, FTIR-RAS, and FE-SEM), sensitive to the surface properties. Effects of atmosphere, temperature, impurity metals on initial oxidation have been made clear.

Presentations

Improving Physicochemical Properties of Anodic Oxide Films on Aluminum by Two-step Electrolysis; H. Konno, Y. Baba, R. Furuichi and K. Yokoyama: The 1994 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Surf. Finish. Soc., and Corros. Eng. Soc., Sapporo, Jan., 1994.

Modeling of Heavy Metal Ion Adsorption on Hematite; H. Tamura, K. Ohkita and R. Furuichi: The 1994 Winter Meeting of the Hokkaido Sections of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1994.

Improving Physicochemical Properties of Anodic Oxide Films on Aluminium Using Chromate Treatment; H. Konno, Y. Baba and R. Furuichi: The 89th Meeting of Surf. Finish. Soc. Jpn., Tokyo, Mar., 1994.

Affinity of Heavy Metal Ions for Ion Exchange Adsorption; H. Tamura and R. Furuichi: The 67th Spring Annual Meeting of Chem. Soc. Jpn., Tokyo, Mar., 1994.

Electrochemical Modification of Alloy Surfaces to Improve Oxidation Resistance at Elevated Temperatures; H. Konno: The 61st Annual Meeting of the Electrochem. Soc. Jpn., Sendai, Apr., 1994.

Improving Oxidation Resistance of Alloys at Elevated Temperatures with Electrochemically Formed Composite Oxide Films; H. Konno: JIM Sympo. on Anti-degradation Properties of New Materials and Coatings at Elevated Temperatures, Tsukuba, May, 1994.

Initial Oxidation of SUS 430 stainless steel at 800-1000°C; I. Saeki, H. Konno and R. Furuichi: JSCE CORROSION '94, Tsukuba, May, 1994.

Improving Corrosion Resistance of Aluminium with Anodic Oxide Films Containing Chromium Ions; H. Konno, Y. Baba and R. Furuichi: *ibid.*

Pyrolytic Process of La(III)-Cr(VI) Precursor for the Perovskite Type Lanthanum Chromium Oxide; A. Furusaki, H. Konno and R. Furuichi: Intl. and III SINO-JAPANESE Sympo. Thermal Measurements, Xi'an, China, June, 1994.

Preparation of "Li Ion Memory" Ion Exchager and Its Properties; A. Uchibo, H. Tamura and R. Furuichi: The 1994 Summer Meeting of the Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Muroran, Jul., 1994.

Analysis of Deoxygenation and Transition Reactions of $LaCrO_4$ by Thermal Analysis; A. Furusaki, H. Konno and R. Furuichi: The 1994 Summer Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., Muroran, Jul., 1994.

Modeling of Ion Exchange Abilities of the Surface of Metal Oxide Particles; H. Tamura: The 1994 Hokkaido Summer Seminar, Sapporo, Aug., 1994.

Modeling of Ion Exchange Reactions on Metal Oxides —Adsorption Affinity of Ions Determined from Model Parameters—; H. Tamura and R. Furuichi: The International Trace Analysis Symposium '94, Hakodate/Sapporo, Aug., 1994.

Formation of Porous Anodic Oxide Films Containing Chromium Ions on Aluminium; H. Konno, Y. Baba and R. Furuichi: 4th Intl. Sympo. Electrochem. Methods in Corr. Reseach, Sesimbra, Portugal, Sep., 1994.

Effect of Manganese on the Initial Oxidation of Type 430 Stainless steels at 1273 K; I. Saeki, H. Konno and R. Furuichi: EMCR '94, Sesimbra, Portugal, Sep., 1994.

Effect of the Electronegativity of Lattice Metal Ions on the Ion Exchange Abilities of Surface Hydroxyl Groups on Metal Oxides; H. Tamura, N. Katayama and R. Furuichi: The 43rd

Annual Meeting of Jpn. Soc. for Anal. Chem., Fukuoka, Oct., 1994.

Formation of Composite Anodic Oxide Films on Aluminium Utilizing Surface Modification of Substrate; H. Konno: The 11th ARS Confernce, Toba, Nov., 1994.

NUCLEAR REACTOR MATERIALS LABORATORY

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Res. Assoc. Dr. T. Mizuno, Res. Assoc.
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Y. Kuroda, Y. Niitu, M. Takano, H. Tamai, A. Fujishima,
H. Kawabe, T. Nakazawa, and H. Saito

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 on UO_2, thermal properties of cesium uranates, and radioactive waste management.

(1) Hydrogen storage alloys as electrodes of the fuel cell, i.e., La-Ni_5 was tested in an aqueous alkaline solutions. Several types of electrodes were prepared in various conditions. All samples were first activated, then pulverized to small particles, mechanically pressed and sintered. The alloy specimens obtained were examined about stability, i.e., disintegration resistance during charge-discharge cycles in the electrolytes, and it is found that the sintered La-Ni_5 alloy, in which Cu was added after activation, is a suitable electrode for the hydrogen storage type fuel cell.

(2) Passivation and pitting of stainless steel were studied by spectrum analysis of fluctuation in corrosion currents and surface film thickness. The shape of the spectra was expressed by a 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, first, estimates of the stability of passive films in the neutral solution and then, prediction of the pit generation. In the passivation process, spectra changed with increasing thickness of film, and slope, n, approached to zero. Even after the addition of Cl^- ions, n was nearly zero, while the

passive film was stable. However, the change in n appeared, ($-1 \leqq n \leqq 0.5$), when the film became unstable, and sporadic tiny pits were detected.

(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 determined at temperatures from 1600 to 2100 K. The diffusion coefficients were in the order of $10^{-15}m^2/s$, though the vapor pressure of Pd is 10^{-3} torr at 1700 K. 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 performance 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 dependencies of the thermal expansion coefficient 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 anticipated 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 likely that the pH and/or redox potential of the pore water in bentonite would be changed by corrosion of iron. In addition, the behavior of sodium ions, which are the main exchangeable cations of bentonite, was investigated. The redistribution of sodium ions induced by corrosion was observed in the bentoniteiron system, and apparent self-diffusion coefficients of sodium ions were determined, using ^{22}Na as a radiotracer. The results also suggested the changes of pH and/or redox potential of the pore water in the bentonite.

(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 conditiion. Relative partial molar Gibbs free energy $\Delta G(H_2O)$ 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 water, 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

Observation of Pitting Corrosion of Stainless Steel by Spectrum Analysis; T. Fukuda, T. Mizuno and H. Ohashi: The 1994 Joint Meeting of the Hokkaido Secs. of Electrocem. Soc., Surf. Finish. Soc., and Corros. Eng. Soc., Sapporo, Jan., 1994.

Cold Fusion Reaction in Gas Atmosphere by Ceramic; T. Mizuno: 6th Research Meeting for Cold Fusion in Solid., Osaka, Jan., 1994.

Migration Behavior of Sodium Ions in Bentonite and Bentonite-Fe System; Y. Imamura, H. Tamai, T. Kozaki, S. Sato, H. Ohashi and J. Takada: 1994 Annual Meeting of Atomic Energy Society of Japan, Tokyo, Mar. 1994.

Heat Generation from Solid-State Electrolyte by Electrolysis in Deuterium Gas; T. Mizuno: The First Conference of New Hydrogen Energy, Tokyo, June, 1994.

Heat Generation Reaction of Proton Conductor Electrolyzed in High Temperature D_2 Gas; T. Mizuno: Meeting at Chemistry Division in Mitsubishi Heavy Industry Co., Nagasaki, Aug., 1994.

Redox State of Corrosion Products of Overpack Material in Bentonite; H. Tamai, Y. Imamura, T. Kozaki, S. Sato and H. Ohashi; 1994 Fall Meeting of Atomic Energy Society of Japan, Sapporo, Sep., 1994.

Diffusion of Tritium in Compacted Bentonite: M. Takano, Y. Torikai, S. Sato and H. Ohashi; *ibid.*

Thermodynamic Properties of Water in Compacted Montmorillonite; Y. Torikai, S. Sato and H. Ohashi: *ibid.*

Effect of Humic Acid Np(V) Sorption onto Goethite(I); Y. Sakamoto, A. Ohashi, S. Nagao, T. Ohnuki, S. Sato, H. Ohashi and M. Senoo: *ibid.*

Effect of Humic Acid on Np(V) Sorption onto Goethite(II); —Sorption Behavior of Np(V) and Humic Acid onto Goethite(II)—;

A. Ohashi, Y. Sakamoto, S. Nagao, T. Ohnuki, S. Sato, H. Ohashi and M. Senoo : *ibid.*

Corrosion of Iron and Migration of Corrosion Products in Compacted Bentonite ; T. Kozaki, Y. Imamura, J. Takada, S. Sato and H. Ohashi : XVIII International Symposium on the Scientific Basis for Nuclear Waste Management, Materials Research Society, Kyoto, Oct., 1994.

Thermodynamic Properties of Water in Compacted Bentonite under External Pressure-free Conditions ; Y. Torikai, S. Sato, S. Sato and H. Ohashi : *ibid.*

Influence of Humic Acid on Sorption of Neptunium(V) on to Soil ; Y. Sakamoto, s. Nagao, T. Ohnuki, M. Senoo, A. ohashi, S. Sato and H. Ohashi : *ibid.*

Excess Heat Generation from Solid State Electrolyte by Electrolysis in D_2 Gas ; T. Mizuno : Second Conference of New Hydrogen Energy, Tokyo, Dec., 1994.

INTERFACIAL ELECTROCHEMISTRY LABORATORY

Prof. Dr. M. Seo, Assoc. Prof. Dr. K. Azumi, Res. Assoc.
Dr. K. Noda, and Secretary J. Fujiwara

Students

K. Shigyo, M. Koike, Y. Hirota, K. Ueno,
Y. Kageyama, and Y. Fujishige

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 corrosion, passivation, anodic oxidation, surface finishing, and surface coating.

(1) Piezoelectric Response to Adsorption of Iodide Ions on Gold Electrode

The changes in surface energy of gold electode in deaerated 1.0 M $NaClO_4$ solutions with and without iodide ions were sensitively detected by using a piezoelectric technique. The potential of electrocapillary maximum or pzc of gold electrode was evaluated from the piezoelectric signal curve. The addition of iodide ions shifted significantly pzc to the less noble direction, indicating the strong contact adsorption of iodide ions. It was found from the iodide concentration dependence of pzc that the Esin-Markov relation held at pzc.

The piezoelectric signals at the high potentials far from pzc suggested the possibility of structural change or phase change of iodine adlayer with sign-reversal of total surface charge density. The model on monolayer formation of AuI was proposed to explain the structural change of iodine adlayer.

(2) Surface Morphology and Luminescence Properties of Porous Silicon Layer

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 optinum preparation condition of PSL for good adherence to the substrate and for good reproducibility of vsible luminescence with high intensity. The surface morphology of PSL was observed with various microscopic techniques (SEM, TEM, AFM, and CLSM). Furthermore, the 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.

(3) Corrosion Rates of Carbon Steel, Pure Iron, and Iron Thin Film in Deaerated Carbonate Solutions

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 rates of pure iron and carbon steel measured by using inductively coupled plasma atomic emission spectroscopy (ICP–AES). The corrosion of carbon steel in alkaline carbonate solutions proceeds with dissolution and precipitation in the active region. The degree of hydration of the precipitated layer on iron thin film was determined by comparing the electric charge and mass change.

(4) Electrochromism of TiN Thin Film in Boric-Borate Solution

The TiN thin film with a thickness of 1 μm was prepared on stainless steel or platinum plate with PVD technique. The cyclic voltammetry of the film was performed in deaerated boric-borate solution of pH 8.4. The surface roughening of the film during the cyclic voltammetry was observed with AFM. The color of the TiN film changed gold to black with a potential step from the potential of oxide layer formation to the potential of hydrogen evolution. The color changes were reversible between two potentials. It seems that this electrochromism is attributed to the oxide layer formed on the TiN film.

(5) Hydrogen Absorption into Palladium

Hydrogen was absorbed into palladium electrode by using galvanostatic polarization under various conditions to obtain high H/Pd ratio. A few kinds materials were examined as a counter electrode. In the case of platinum and palladium counter electrodes, the dissolution of counter electrodes and the re-deposition onto palladium used as working electrode occur at the cathodic polarization current density higher than $-100\,\mathrm{mA\,cm^{-2}}$. After the long term polarization (>10 ks), the deposition of these metals affects the H/Pd ratio by covering the electrode surface or increasing roughness resulting in reducing effective current density. Graphite electrode was also examined as a counter electrode. After the long term polarization, however, the surface of graphite electrode begins to collapse, and the small powders of graphite deposited onto palladium decreases the current density of hydrogen evolution on palladium electrode.

(6) Resistmetry of Thin Titanium Electrode

Titanium film with ca. $0.5\,\mu\mathrm{m}$ thickness was deposited onto quartz glass plate by using a magneto-electron sputtering technique. Two wires were attached to both sides of the sample to measure the resistance of titanium layer during electrochemical polarization by means of an alternative current (AC) method. The resultant resistance was found to be influenced by the nature of the passive film such as thickness, electric conductivity, and formation of space charge layer. The resistance response is also dependent of the frequency of AC. For example, the space charge layer responds mainly to the frequency of around 1 Hz. The surface morphology of titanium film was also observed by AFM and was found out to be composed of granular structure whose shape changed considerably depending on anodic polarization potential.

(7) Other Activities

Dr. K. Azumi came back to the laboratory, the end of January, after his work as visiting researcher for 17 months at Dept. of Materials Sci. and Eng., Stanford University, California, USA.

Prof. M. Seo attended Japan-USA Seminar on Development and Environmental Characteristics of New Materials which was held in Timberline Lodge, Oregon, USA, June 7-9, 1994 and presented a paper entitled "A QCM Study on Corrosion of Iron Thin Films in Neutral Aqueous Solutions". Prof. M. Seo visited again

USA to conduct the Collaborative Research on "Microscopic In-situ Evaluation of Corroding Surface of Film" with Profs. W. H. Smyrl and M. D. Ward at the Corrosion Research Center, University of Minnesota, Minneapolis, July 3-9. Afterward, he attended the Gordon Research Conference on Wet Corrosion which was held in New London, New Hampshire, July 10-15.

Prof. M. Seo attended the 5th International Symposium on Electrochemical Methods in Corrosion Research (EMCR '94) which was held in Sesimbra (Liboa), Portugal, September 5-8 and presented a Key Note Lecture entitled "An EQCM Study on Corrosion of Iron Thin Film in Deaerated Neutral Solutions". Afterward, he visited Dr. H. Takenouti, Universite Pierre et Marie Curie, Paris and Prof. P. Marcus, Ecole Nationale Superieure de Chimie de Paris, France, September 12-13. Furthermore, Prof. M. Seo attended the 4th Joint Conference of University of Science and Technology Beijing and Hokkaido University, which was held at University of Science and Technology Beijing, Beijing, China, October 18-22 and presented a paper entitled "Application of EQCM to Corrosion of Iron Thin Film in Deaerated Neutral Solutions".

Dr. K. Azumi visited the Corrosion Research Center, University of Minnesota, Minneapolis, USA, November 6-19, to conduct the Collaborative Research with Profs. W. H. Smyrl and M. D. Ward.

The following foreign scientists visited this laboratory: Prof. Su-il Pyun, Dept. of Materials Sci. and Eng., Korea Advanced Institute of Science and Technology, Daejon, Korea, on Jan. 5-Feb. 3, Prof. C. K. Ong, Dept. of Physics, National University of Singapore, Singapore, on Feb. 23-March 1, Prof. C. Leygraf, Dept. of Materials Sci. and Eng., Royal Institute of Technology, Stockholm, Sweden, on June 19-27, Dr. J. H. Nordien, Norway Insitute of Technology, Norway, on June 23-24, Dr. P. D. Green, Dept. of Metallurgy and Materials Sci., The University of Nottingham, U. K., on Aug. 22, Prof. W. H. Smyrl, Dept. of Chem. Eng. and Materials Sci., University of Minnesota, Minneapolis, USA, on Sept. 26-Oct. 6.

Presentations

QCM Study on Active Dissolution of Iron Thin Film ; K. Yoshida, K. Noda and M. Seo : The 1994 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Surf. Finish. Soc., and Corros. Eng. Soc. Sapporo, Jan., 1994.

Electrochemical Etching of p-Type Si in HF Solution and Surface Morphology ; K. Shigyo, H. Takahashi and M. Seo : *ibid.*

Surface Morphology and Photo-Electrochemistry of Porous Si ; K. Shigyo, H. Takahashi and M. Seo : The 89th Annual Meeting of Surf. Finish. Soc. Jpn., Tokyo, Mar. 1994.

Photo-Electrochemical Behavior of TiN Thin Films ; M. Seo, S. Watanabe and K. Azumi : The 127th Spring Meeting of Iron and Steel Inst. Jpn., Tokyo, Mar, 1994.

Improvement of Piezoelectric Detection and Its Application to UPD of Ag on Au ; M. Seo, Y. Yamamoto and K. Noda : The 61st. Meeting of Electrochem. Soc. Jpn., Sendai, Apr. 1994.

Polarization Behavior of Carbon Steel in Deaerated Carbonate Solutions ; K. Noda, Y. Hirota and M. Seo : '94 Spring Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1994.

A QCM Study on Corrosion of Iron Thin Films in Neutral Aqueous Solutions ; M. Seo, K. Yoshida and K. Noda : Japan-USA Seminar on Development and Environmental Characteristics of New Materials, Timberline Lodge, Oregon, USA, June, 1994.

Electrochemical Behavior of Carbon Steel in Carbonate Solutions ; K. Noda, Y. Hirota and M. Seo : The 1994 Summer Meeting of Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Muroran, July. 1994.

An EQCM Study on Corrosion of Iron Thin Film in Deaerated Neutral Solutions ; M. Seo, K. Yoshida and K. Noda : The 5 th International Symposium on Electrochemical Methods in Corrosion Research (EMCR '94), Sesimbra (Lisboa), Portugal, Sept., 1994.

Electrochromism of TiN Electrode ; K. Azumi, Y. Kageyama, M. Seo, S. Watanabe and Y. Inokuti : The 90 th Annual Meeting of Surf. Finish. Soc. Jpn., Sapporo, Oct., 1994.

Fundamental Study on Double Zincate Treatment of Alminium Alloys; K. Azumi, H. Takahashi, M. Seo and L. Nanis, *ibid.*

QCM Measurement of Corrosion Behavior of Iron Thin Films in Deaerated Carbonate Solutions; Y. Hirota, K. Noda and M. Seo: *ibid.*

Surface Morphology and EL Behavior of Porous Si with Different Specific Resistivities; K. Shigyo, K. Azumi, H. Takahashi and M. Seo: *ibid.*

Influence of Corrosion Products on Metabolism of Sulfate Reducing Bacteria; F. Baba, T. Suzuki and M. Seo: The 41 st. Discussion Meeting of Jpn. Soc. Corros. Eng., Matsuyama, Oct., 1994.

Application of EQCM to Corrosion of Iron Thin Film in Deaerated Neutral Solutions; M. Seo, K. Yoshida and K. Noda: The 4 th Joint Conference of University of Science and Technology Beijing and Hokkaido University, Beijing, China, Oct., 1994.

DISSIMILAR MATERIALS INTERFACE ENGINEERING LABORATORY

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

Students

S. Kawamori, M. Noguchi, T. Yoshioka, F. Christian,
M. Narumi, S. Hata, M. Mukaihira, K. A. Zaini, T. Toyama,
R. Masumoto, T. Watanabe, M. Nakano, T. Sugawara,
A. Tomita, H. Fujimoto, H. Murakoshi, and T. Yamamoto

Prof. T. Sugawara from Fukushima National College of Technology stayed at our laboratory as a visiting researcher from April 1994 to March 1995. Mr. Y. Tu from China joined our laboratory as a research associate and he is investigating on the high temperature sulfidation of nickel-based alloys.

Associate Professor Ohsasa visited Germany on July 3-9 to attend the International workshop on SHORT-TERM EXPERIMENTS UNDER STRONGLY REDUCED GRAVITY CONDITION held in Bremen. Professor Narita attend the 4th Conference of University of Science and Technology Beijing and Hokkaido University held in Beijing, China in November.

The research programs in our laboratory are as follows:

(1) Ceramic-Metal joining

Aluminum nitride and silicon nitride ceramics were joined to metals using active alloy solders such as Ni-Cu-Ti, Ag-Cu-Ti, and Ag-Cu-In-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-exchaged 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 andAl–Si molten alloys, and the optimum condition was investigated to make a 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 Method and their mechanical and physical properties were investigated.

(7) Molecular dynamic 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

On the Multi-phase Sulfide Scale formed in Fe–Cr Alloy; M. Noguchi and T. Narita: The 1994 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Surf. Finish. Soc. and Corros. Eng.

Soc, Sapporo, Jan., 1994.

Limit of Fraction Solid for Liquid Flow during Alloy Solidification : K. Ohsasa and M. Kudoh : The 127th Annual Meeting of ISIJ, Tokyo, Apr., 1994.

On the Governing Factors in the Strength of Ceramic-Metal Joints ; T. Narita : Subcommittee Seminar of JIM, Tokyo, Apr., 1994.

History and Future Trends in Development of Ceramic-Metal Joints; T. Narita : Toyama Prefecture University Open Seminar, Toyama, Apr., 1994.

Effect of the Strength of Ceramics on Fracture Strength of Joints ; S. Hata and T. Narita : The 114th Annual Meeting of JIM, Tokyo, Apr., 1994.

Low Temperature Joining of Aluminum Nitride and Metals by Using Active Alloy Solders ; M. Mukaihira and T. Narita : *ibid.*

Diffusional Analyses of Cation Distribution in Sulfide Scale on Fe-Cr Alloy ; M. Noguchi and T. Narita : *ibid.*

Internal Sulfidation Behavior in Fe-Cr-Ti(Nb)-C Alloy ; S. Kawamori and T. Narita : *ibid.*

Effect of Si Addition on High Temperature Sulfldation in Ti-Al Intermetallic Compounds ; T. Yoshioka and T. Narita : *ibid.*

High Temperature Oxidation Behavior in Splayed Heat-resistant MCrAlY Coating ; H. Taumi and T. Narita ; *ibid.*

Analysis of Solidification Path of Aluminum Based Casting Alloys ; K. Ohsasa, T. Ohmi, M. Kudoh and T. Narita : Hokkaido Section Meeting of Jpn. Foundrymen's Soc., Sapporo, May, 1994.

Ultrasonic Micro-Spectroscopy of Ag-ion Diffused Glasses ; K. A. Zaini and T. Narita : The 93 Hokkaido Section Summer Meeting of JIM, Sapporo, June, 1994.

Effect of Preliminary Pressure Addition on the Strength of Ceramic-Metal Joints ; T. Motoyama and T. Narita : *ibid.*

On the Growth Process of Alloy Layer in Galvanized Ferrous with Zn-Al Alloy ; R. Masumoto, J. Tanaka and T. Narita : *ibid.*

High Temperature Nitriding Properties of Ti-Al Alloys ; T. Watanabe, K. Ohsasa and T. Narita : *ibid.*

Molecular Dynamics Simulation of Grain Boundary Formation of

Iron T. Toyama, K. Ohsasa and T. Narita: *ibid.*

Analysis of Solidification Path of Alloy; K. Ohsasa: The 14th Meeting of Solid Ionics Soc., Sapporo, Aug., 1994.

High Temperature Oxidation Behavior of Plasma Splayed MCrAlY Coatings; H. Taumi and T. Narita: The 115th Annual Meeting of JIM, Fukuoka, Oct., 1994.

Nitridaton Process in Ti-Al-Si Alloy; T. Watanabe, K. Ohsasa and T. Narita: *ibid.*

Effect of Pd Addition on Ni-Cu-Ti Solder in Si_3N_4/Metal Joinings; K. Miyama, M. Itoh and T. Narita: *ibid.*

Joining of Aluminum Nitride and Metals by Using Active Alloy Solder; M. Mukaihira and T. Narita: *ibid.*

Interdiffusion Coefficient and Non-stoichiometry in $(Fe, Cr)1-\delta$ S; M. Noguchi and T. Narita: *ibid.*

Characterization of Ag-ion Diffused Glasses with Ultrasonic Microscope; K. A. Zaini and T. Narita: *ibid.*

Modification of Phase Structure of Galvanized Layer in Ferrous Materials; R. Masumoto, J. Tanaka and T. Narita: *ibid.*

Analysis of Solidification Path of Fe-Cr-Ni Ternary alloys; K. Ohsasa, S. Nakaue, K. Kudoh and T. Narita: The 128th Annual Meeting of ISIJ, Fukuoka, Oct., 1994.

Development of Silicon Nitride Ceramics-Metal Joints with High Fracture Strengths and the Related Factors; T. Narita and S. Hata: The 4th Conference of University of Science and Technology Beijing and Hokkaido University, Beijing, Nov., 1994.

INTERFACE MICRO-STRUCTURE ANALYSIS LABORATORY

Prof. Dr. H. Takahashi, and Assoc. Prof. Dr. K. Kurokawa

Students

Y. Li, K. Nukui, M. Shikanai, and F. Takashima

The laboratory was newly founded in June, 1994, according to the rearrangement of organization of Faculty of Engineering, Hokkaido University. Prof. H. Takahashi was promoted from Assoc. Professor at the Electrochemistry Laboratory in the corrosion research group, and Assoc. Prof. K. Kurokawa joined from the Metals Research Institute, Hokkaido University.

The research activity of the laboratory is directed to a 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) Cathodic polarization of aluminum covered with anodic oxide films.

Cathodic polarization behavior of aluminum covered with barrier anodic oxide films has been examined under potentiostatic conditions in H_2SO_4, Na_2SO_4, $H_2SO_4/CuSO_4$ solutions. In the H_2SO_4 solution, hydrogen evolution was only a reaction during cathodic polarization, while in the Na_2SO_4 solution the film breakdown and pit formation took place in addition to hydrogen evolution. In the $H_2SO_4/CuSO_4$ solution, Cu deposition was observed at the weak spots locally.

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

Aluminum specimens covered with porous anodic oxide films were immersed in $H_2SO_4/CuSO_4$ solutions and irradiated a pulse YAG laser through quartz window. After laser irradiation, the specimen was cathodically polarized under potentiostatic conditions.

Copper layer was found to deposit at laser irradiated area.

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

Aluminum specimens covered with porous anodic oxide films were immersed in Ti^{4+} solutions and then heated in air to deposit TiO_2 in the pore. After heat treatment, the specimen was anodized in a neutral borate solution to fill the pores with Al_2O_3. The effect of pore-widening and the repetition of TiO_2 deposition process on the dielectric properties of pore-filled anodic oxide films was examined. The parallel capacitance of the oxide film formed by the pore-filling method was larger by 40% than that of oxide films without TiO_2 deposition. Rutherford back scattering spectroscopy showed that TiO_2 distributes only in the outer part of oxide films.

(4) Formation and breakdown of anodic 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. In boric acid/borate solutions, breakdown of anodic oxide films took place at 400–500 V, and this was due to the formation of crystalline oxide with voids at the middle of oxide layer. In the boric acid solution, the formation of anodic oxide films was observed until 1180 V with growth of imperfections during anodizing.

(5) 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 the second phase such as additives and reinforcement materials.

(6) 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 growth rate of the reaction layer decreased in the order of the reaction mode

(A), (B) and (C). The maximum application temperature of Fe, Co and Ni-based alloys/SiC composites for a hot machinery was estimated to be about 1200 K. Furthermore, the investigation in metal/Si_3N_4 systems is also in progress.

(7) Bonding of $MoSi_2$ to graphite.

As a basic research for the improvement of the oxidation resistance of C/C composite, the experiments on 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 August, Prof. Takahashi attended the 7th International Symposium on Passivity at Technical University of Clausthal in Germany to present a paper entitled "Film Breakdown and Pit Formation during Cathodic Polarization of Aluminum Covered with Anodic Oxide Films. —Effect of Film Structure—, and during his stay in Europe he visited Prof. A. Rauscher at Szeged University in Hungary, and Profs. H. Takenouchi and P. Marcus at University of Pierre et Marie Curie in France. On October, he attended the 186th meeting of the Electrochemical Society at Miami in Florida to present a paper entitled "Local Anodizing of Aluminum in Sulfuric Acid Solution with Laser Irradiation". After the meeting he visited Prof. W. H. Smyrl at the University of Minnesota in Minneapolis and had a good opportunity to discuss with Profs. M. D. Ward, R. A. Oriani, and D. A. Shores and to do experiments.

Assoc. Prof. Kurokawa visited Thailand in January to give lectures on high temperature oxidation of metals and alloys at Chiang Mai University and on oxidation resistance of ultra-high temperature materials at Chulalongkorn University, King Mongkuts Institute of Technology Thonburi, and Thailand Institute of Scientific and Technological Research.

Foreign researchers visited the laboratory were Prof. S. Thongtem, Chian Mai University in April, Mr. J. H. Nordlien, the University of Tokyo in July, and Prof. W. H. Smyrl, the University of Minnesota in September.

Presentations

Effect of Laser Irradiation on The Formation of Anodic Oxide Films on Aluminum; K. Nukui, H. Takahashi, M. Seo, M. Kawasaki and Y. Matsui: The 1994 Joint Meeting of the Hokkaido Secs. of Electrochem. Soc., Surf. Finish. Soc., and Corros. Eng., Soc., Sapporo, Jan., 1994.

Cathodic Polarization of Aluminum Covered with Composite Oxide Films; K. Fujiwara, H. Takahashi and M. Seo: *ibid.*

Subjects in Oxidation Resistance of $MoSi_2$; K. Kurokawa and H. Uchiyama: *ibid.*

Formation Mechanism of Anodic Oxide Films on Aluminum under The Laser Irradiation; K. Nukui, H. Takahashi, M. Seo, M. Kawasaki, and Y. Matsui: The 89th Annual Meeting of Surface Finishing Soc. Jpn., Tokyo, Mar., 1994.

Bonding of $MoSi_2$ to Graphite by the SPS Method; K. Kurokawa, T. Horibe, H. Uchiyama, T. Nagai, T. Okutani and Y. Nakata: The 114th Annual Meeting of JIM, Tokyo, Mar., 1994.

Oxidation Resistance of SiO_2-Forming Materials; K. Kurokawa, M. Ueki and Y. Satoh: *ibid.*

Oxidation Behavior of Dense $MoSi_2$-WSi_2 Solid Solutions; K. Kurokawa, T. Matsuoka and T. Nagai: *ibid.*

Local Breakdown Mechanism of Anodic Oxide Films on Aluminum during Cathodic Polarization; K. Fujiwara, H. Takahashi and M. Seo: '94 Spring Meeting of Jpn. Soc. Corros. Eng., Tsukuba, May, 1994.

High Temperature Oxidation of Silicides; K. Kurokawa: JIM Symp. on Corros. Resist. of New Maters. and New Coating, Tokyo, May, 1994.

Bonding of $MoSi_2$ to Graphite; T. Horibe, K. Kurokawa, T. Nagai, T. Okutani and Y. Nakata: The Summer Meeting of Hokkaido Secs. of JIM and ISIJ, Sapporo, June, 1994.

Oxidation Property of Dense $MoSi_2$-WSi_2 Solid Solutions; T. Matsuoka, K. Kurokawa and T. Nagai: *ibid.*

Formation of Ti/Al Composite Oxide Films on Aluminum by Pore-Filling Method; M. Shikanai, H. Takahashi and M. Seo:

The '94 Summer Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Muroran, July, 1994.

Film breakdown And Pit Formation during Cathodic Polarization of Aluminum Covered with Anodic Oxide Films. —Effect of Film Structure— ; H. Takahashi, K. Fujiwara and M. Seo : The 7th intern. Symp. of Passivity, Clausthal (Germany), Aug., 1994.

Local Plating on Aluminum with Laser Irradiation ; K. Nukui, H. Takahashi, M. Seo, M. Kawasaki and Y. Matsumi : The 90th Annual Meeting of Surface Finishing Soc. Jpn., Sapporo, Sept., 1994.

Incorporation of TiO_2 into Anodic Oxide Films on Aluminum by Pore-Filling Method ; M. Shikanai, H. Takahashi and M. Seo ; *ibid.*

Surface Treatment of V-based alloys by SiC Pack-Cementation ; K. Kurokawa : *ibid.*

Local Anodizing of Aluminum in A Sulfuric Acid Solution with Laser Irradiation ; K. Nukui, H. Takahashi, M. Seo, Kawasaki and Y. Matsumi : The 186th Meeting of the Electrochem. Soc., Miami, U.S.A., Oct., 1994.

High Temperature Oxidation of Disilicides ; K. Kurokawa : The 115th Annual Meeting of JIM, Fukuoka, Oct., 1994.

High Temperature Oxidation of $MoSi_2$ in Low and Medium Temperature Regions ; K. Kurokawa and H. Uchiyama : *ibid.*

Formation of Anodic Oxide Films and Cu-Plating on Aluminum at Selected Area with Laser Irradiation ; H. Takahashi and K. Nukui : The 11th ARS Symp. in Toba, Kashikojima, Nov., 1994.

Application of Laser Technology to Surface Finishing of Aluminum ; H. Takahashi : The 2nd Seminar of Hokkaido Surface Finishing Research Institute, Sapporo, Nov., 1994.

Pit Formation on The Aluminum Covered with Anodic Oxide Films during Cathodic Polarization. —Where is the Precursor of Pitting ?— ; H. Takahashi, K. Fujiwara, F. Takashima, M. Seo, M. Al-Odan, W. H. Smyrl : Seminar on Environment and Materials, Sendai, Dec., 1994.

Solid-State Reaction and Structure in Ceramic-Metal Interface; H. Takahashi and K. Kurokawa: The NSG Found. Mat. Sci. Meeting, Tokyo, Dec., 1994.

High Temperature Oxidation of Silicides and its Subjects; K. Kurokawa: The JSCE 101st Symp. on Corros. Resist. of Intermetallic Compounds at High Temperature Environment, Tokyo, Dec., 1994.

Ant's Nest Corrosion of Copper Tubing

Takenori Notoya

Kindai Bungei Sha Publishing Company
PP. 1-65 (1994).

An unusual form of copper tube corrosion has been detected early in service and even also in leakage tests after manufacturing. The morphology of this corrosion is similar to an "ant's nest" when viewed in cross-section under a microscope. The corrosion was found to be promoted by carboxylic acids resulting from the hydrolysis of chlorinated organic solvents used to degrease the tubes and by self-evaporating lubricant oils used in the hairpin-bending process. This corrosion can be simulated in vitro in a humid atmosphere in the presence of a small amount of carboxylic acid. Corrosion initiated at inner surfaces of copper tubes can be prevented by pretreatment of the inner surfaces, such as hot air-drying after steam cleaning to remove organic detergents and lubricants which were remained in the tubes. At outer surfaces, the corrosion can also be prevented by surface treatment of copper tubes with organic inhibitors. This book presents cases of the premature failure of copper tubes, simulation tests, corrosion mechanisms and the preventive measures. (Japanese)

Galvanic Corrosion of Steel-Copper System in Closed Fresh Water

T. Notoya

Jounal of the Japan Copper and Brass Research
Association **33**, 56-61 (1994).

Galvanic corrosion current was measured using a zero resistance ammeter for a galvanic couple consisting of copper-steel electrodes in tap water and a 10 ppm Cl-solution under closed-stagnant conditions at 25°C. The net current resulted from an anodic reaction of iron dissolution. In addition, the cathodic reduction reaction of oxygen on the copper electrode dropped dramatically in a short time due to the consumption of dissolved oxygen in these solutions. A weight loss measurement was also conducted for the steel coupled with two different sizes of copper to determine the galvanic corrosion rate of steel under the stagnant conditions. The corrosion rate of steel decreased sharply in a week and remained at a small value in the closed systems. From this it is concluded that the steel pipes coupled with copper tubes do not cause any serious galvanic corrosion problems such as leakage and/or clogging of pipes containing corrosion products in sprinkler systems. (Japanese)

A Study of the Electrochemical Formation of Cu(I)-BTA Films on Copper Electrodes and the Mechanism of Copper Corrosion Inhibition in Aqueous Chloride/ Benzotriazole Solutions

A. D. Modestov, G.-D. Zhou, Y.-P. Wu, T. Notoya
and D. P. Schweinsberg

Corrosion Science, **36**, [11], 1931-1946 (1994).

Cu electrode behavior in Cl^- and benzotriazole (H-BTA) containing acidic or neutral solution was studied by volummetrey photocurrent response, impedance measurements and chemical analysis of BTA content in passive layers. It was shown that the rate of formation of Cu-BTA films in acidic solutions is controlled by the transport of $CuCl_2^-$ ions through pores in the film at an early stage of film formation and later by the volume diffusion rate in the film. The photocurrent measurements have revealed that Cu-BTA film formation is accompanied by the simultaneous deposition of a Cu_2O underlayer. The main portion of the polarization resistance of the passive layer was ascribed to the Cu_2O underlayer. It is proposed that the role of the Cu-BTA overlayer is to stabilize the Cu_2O underlayer and maintain its high resistance by preventing it from bring doped by Cl^- ions resulting in the formation of solid CuCl on top of the Cu_2O. (English)

Dissolved States of Divalent Metal Chlorides in $AlCl_3$-NaCl Melts

T. Ishikawa, T. Sasaki, S. Konda
and M. Noguchi

Proc. 9th Int. Symp. Molten Salts, PV 94-13, p. 164-170, The Electrochemical Society (1994).

Solubilities of the divalent metal chlorides, $MnCl_2$ $MgCl_2$, $CdCl_2$, $CoCl_2$ and $PbCl_2$, in binary chloride melts ($AlCl_3+NaCl$) were measured in the concentration range from 55 to 59 mol% of $AlCl_3$ at 200°C. The equilibrium constants for dissolution were derived as a function of solubilities and the mole fraction of $AlCl_3$ on the assumption of the dissolution reaction being $Al_2Cl_7^- + 1/2MeCl_2(s) = 1/2Me^{2+} + 2AlCl_4^-$.

The equilibrium constants calculated from experimental results suggest that divalent metal chlorides dissolve in the melts as free Me^{2+} cations forming complex anions. (English)

Fundamental Studies on High-Temperature Molten Salts for Electrorefining of Liquid Aluminum

Mikito Ueda, Shoichi Konda, Takeshi Sasaki
and Tatsuo Ishikawa

Proc. 5th China-Japan Bilateral Conference on Molten
Salt and Technology, p. 148–151 (1994).

For the electrorefining of Al from aluminum scraps by using a bipolar electrode system, characteristic of $BaCl_2$–NaCl melts which are less-corrosive to cell materials than fluoride melts were investigated. Measurement of densities indicated that the melts containing $BaCl_2$ over 50 mol% had higher densities than that of liquid Al (2.35) and were applicable to the system. Next, methods for introducing aluminum component into $BaCl_2$–NaCl melts were examined in terms of their solubilities. The results suggested that only the melts fed with double salts of AlF_3–NaF were available for the electrolysis bath, because of a significant concentration of aluminum component in the melts. (English)

Large Undercooling and Macrostructure of Iron-based Alloys

Masayuki Kudoh, Jun-ichi Tanaka
and Ken-ichi Ohsasa

U. S.-Japan Cooperative Science Program Seminar
on "Solidification Processing for the 21st
Century", 33-42 (1994).

A high degree of undercooling before solidification of alloys is available for the improvement of material quality. In this study, a new method for controlling the undercooling of 0.20 pct.C steel and of iron-based alloys was examined by using a flux composed of oxides, and the optimum oxide content of the flux for obtaining a high degree of undercooling wss determined. A degree of undercooling up to about 232 K was obtained by using this method. We called this undercooling "static undercooling". For the carbon steel, as the undercooling was increased, the dendrite became fine, the microsegregation was reduced, and the hardness profile was uniform, However, the degree of undercooling for iron-based binary alloys depended on the kinds of solute elements and increased in order of Al, C, Si, Cr, Ni, and Mn. The microstructure of the binary alloys became fine and showed a ductile fracture surface with the increase in the undercooling. Furthermore, a mechanism of static undercooling obtained by this method was suggested by investigating the effect of the solute element on the undercooling for the carbon steel and for the iron-based binary alloys.

(English)

Undercooling and Solidification Behavior of Fluid Clumps of Second-Poured Melt of Hypereutectic Al-Si Plloy in Duplex Casting Arocess

Tatsuya Ohmi, Masayuki Kudoh, Ken-ichi Ohsasa,
Youichi Itoh, Kiyotaka Matsubara
and Kuniyoshi Ishii

J. JILM, 44, 91-96 (1994).

The primary silicon crystals of hypereutectic Al-Si alloys are reported to be refined by the Duplex Casting Process (a two-step casting of two molten alloys with different composition ; i.e., "the first alloy" with lower liquidus temperature and "the second alloy" with higher liquidus temperature). Recently, concerning the refining mechanism, the authors have proposed that copious nucleation of primary silicon crystals takes place in the second alloy which is rapidly cooled and highly undercooled during mixing with the first alloy. The purpose of this study is to investigate the degree of undercooling and the solidification behavior of the fluid clumps of the second alloy which are thought to form the clustering structures of fine primary crystals. The relationships between the degree of undercooling and the primary silicon size of Al-32 mass%Si and Al-22 mass%Si alloys were obtained by use of three solidification techniques : (1) air-cooling or immersion into a metal bath of melt-filled graphite crucible, (2) casting in a wedge-shaped copper mold, and (3) melt-injection into a lead bath. The primary silicon size of the finest cluster observed in the ingot produced by the Duplex Casting process with the combination of Al-12 mass%Si alloy and Al-32 mass%Si alloy is 15 μm, and the corresponding undercooling is estimated at 243 K. (Japanese)

A Unidirectionally Solidified Structure of an Immiscible Alloy of Zn-Pb under Microgravity

Masayuki Kudoh, Tohru Noguchi
and Ken-ichi Ohsasa

Metallurgical Processes for the Early Twenty-First
Century Vol. 1, Tms., 245-253 (1994).

The solidification of an immiscible Zn-Pb alloy to examine the phase separation behavior under microgravity was conducted in the drop shaft facility located in Kamisunagawa, Japan. The facility has a low-gravity time of 10 s in an acceleration of 10^{-4} g. A specimen inserted into a graphite crucible was cooled from the bottom by partially immersing the crucible into a melt of lower melting temperature. The acceleration of gravit was reduced 5 s after the onset of cooling by dropping a capsule. Lead droplets formed in a low-g zone were small, since their growth was controlled by the diffusion of solute in the melt. The frequency of droplet formation was small, making it impractical to obtain a dispersed structure of the lead droplets in the immiscible alloy. (English)

The Cathodic Polarization of Aluminum Covered with Anodic Oxide Films in a Neutral Borate Solution

—I. The Mechanism of Reaction—

Hideaki Takahashi, Koichi Kasahara,
Kazutoshi Fujiwara and Masahiro Seo

Corrosion Science, **36**, 677-688 (1994).

Aluminum covered with barrier type anodic oxide films was polarized anodically and cathodically in a neutral borate solution in a vacuum to investigate rectification phenomena. Rectification took place only in the solution, suggesting that it is due to a high rate of proton reduction during cathodic polarization. Potentiostatic cathodic polarization in solution showed a threshold potential of −2.0 V (Ag/AgCl). At more positive potentials, a minute cathodic current flows, while the current increases with time below −2 V (Ag/AgCl). The increase in current was accompanied by hydrogen evolution at weak spots in the oxide film, causing the formation of a small number of pits. The mechanism of pit formation is discussed in terms of alkalization at the bottom of pits. (English)

The Cathodic Polarization of Aluminum Covered with Anodic Oxide Films in a Neutral Borate Solution

—II. Film Breakdown and Pit Formation—

Hideaki Takahashi, Kazutoshi Fujiwara
and Masahiro Seo

Corrosion Science, **36**, 689-705 (1994).

Porous and barrier type oxide films were formed anodically on pure aluminum and dissolved chemically. The specimens were then cathodically polarized by the potential sweep method in a neutral borate solution. It was found that the cathodic current starts to increase at about -2 to -3 V (Ag/AgCl) and that at more negative potentials it increases almost linearly, accompanied by hydrogen evolution. The cathodic polarization curve shifts in the anodic direction with decreasing film formation potential and increasing chemical dissolution time. During cathodic polarization, cubic-shaped pits are formed by local corrosion of the metal substrate. The number of pits formed by cathodic polarization is larger for porous than for barrier type oxide films, while the pit number is independent of the film formation potential, it increases considerably with increasing chemical dissolution time. The ratio of the local corrosion rate to the electrochemical reaction rate during cathodic polarization is about 0.03 on specimens without chemical dissolution, and about 0.10 with chemical dissolution. The effect of film structure on the pit formation during cathodic polarization is discussed in terms of imperfections in the oxide. (English)

Anodizing of Aluminum Coated with Thermal Oxide Films
—Effect of Anodizing Temperature on the Formation of Anodic Oxide Films—

Hideaki Takahashi, Mitsugu Dairaku,
and Masahiro Seo

J. Surface Finishing Soc. Jpn., 45, 60-67 (1994).

High-purity aluminum specimens were subjected to heat treatment at 823 K for 3 h in air, and anodized galvanostatically at $T_a=293-353$ K with a constant current density in a neutral borate solution, and the effects of anodizing temperature (T_a) on the formation and dielectric properties of the anodic oxide films were examined.

During anodizing, the rate of increase in anode potential, dE_a/dt_a, was found to be much larger for specimens that were subjected to heat treatment than for those that were not, reaching a maximum at $T_a=313-333$ K. The Al^{3+} dissolution current for the heated specimens was smaller than that for unheated specimens at all values of T_a, and increased considerably with increasing T_a.

At all values of T_a except 353 K, the anodic oxidie films formed after thermal oxidation were composed of three layers: an outer amorphous oxide layer (thickness δ_0), a middle crystalline oxide layer (δ_c), and an inner amorphous oxide layer (δ_i). With increasing T_a, the δ_0 and δ_i decreased but δ_c increased. At 353 K, the film formed after thermal oxidation showed a single layer of crystalline oxide.

The dielectric properties of thermal/anodic oxide films changed considerably with T_a and E_a, and this was understood to be due to penetration of the electrolyte solution into voids in the oxide films.

The mechanism of film formation during anodizing after thermal oxidation is discussed in terms of the crystallization and electrochemical dissolution of the amorphous oxide layers. (Japanese)

Electrochemical Analysis of Imperfections in Anodic Oxide Films on Aluminum

Hideaki Takahashi and Kazutoshi Fujiwara

J. Surface Science Soc. Jpn., **15**, 433-439 (1994).

The Formation of imperfections in anodic oxide films on aluminum and the analysis of the imperfection by electrochemical method are reviewed.

Imperfections included in anodic oxide films are originated from impurities in the metal substrate, rough surface of specimens, and the field assisted crystallization of amorphous oxide films during anodizing. Imperfections included in barrier type oxide films formed on highly pure aluminum are due to the rough surface, while those in composite oxide films formed by hydrothermal treatment/anodizing and thermal treatment/anodizing are mainly due to the crtstallization of oxide.

Cathodic polarization in a neutral borate solution is proposed as a method for estimation of the number of imperfections in the oxide film. (Japanese)

Anodic Oxidation of Valve Metals and Structure of Anodic Oxide Films

Masahiro Seo

J. Surf. Finish. Soc. Japan, 45, 377-382 (1994).

This article reviewed the anodic oxidation behavior of valve metals and the structure, composition and functions of their anodic oxide films. The discussion was made on the differences in kinetics of anodic xoidation and film properties (electronic, optical, and chemical) between valve metals. The special attentions were paid on the differences between Ti, Ta, Al, and Si. (Japanese)

Improving the Mechanical Properties of Anodic Oxide Films on Aluminum Utilizing Mo-Oxyhydroxyde Films

Kazuo Yokoyama, Hidetaka Konno,
Yuko Baba and Ryusaburo Furuichi

Hyomen Gijutsu (J. Surf. Finish. Soc.
Jpn.), **45**, 1026–1028 (1994).

It was found that a two-step anodizing process to from porous oxide films on aluminum, consisting of cathodic deposition of Mo(V)-Mo(VI) mixed oxyhydroxide films on aluminum from an ammonium molybdate solution followed by anodizing of the aluminum in acid solutions, results in films having improved mechanical properties. Anodic oxide films formed in a sulfosuccinic acid solution by the present process showed an increase in Vickers hardness of about 20% and the best results were $Hv_{50}=690\pm 23$ $(\pm 1\sigma)$ for cross section. The process is being extended using chromate treatment in the first step, and further improvements in physicochemical properties are expected. (Japanese)

Solid-State Reaction and Structure in Ceramic-Metal Interface

H. Takahashi and K. Kurokawa

NSG Found. Mat. Sci. Eng. Rep.,
No. 12, 99-106 (1994).

The kinetics and mechanism of solid-state reaction between metals and silicon nitride at high temperatures were investigated. Main purpose in the present study is to establish the thermodynamical condition for avoidance of the formation of brittle silicides in the metal-silicon nitride interface.

In the Ni–Si_3N_4 reaction system, only a solid solution layer is formed without a formation of any silicide at the temperatures below 1373 K and the growth of the reaction layer obeys a linear rate law. Therefore, the rate determining step in the system was speculated to be the decomposition reaction of silicon nitride. On the other hand, in the Fe–Si_3N_4 and Co–Si_3N_4 systems, the temperature range where the reaction layer consisting of a solid-solution is formed is extremely limited. From these results, the mechanism of solid-state reaction between metal and silicon nitride, especially in Ni–Si_3N_4 system, is discussed. (Japanese)

High Temperature Oxidation of Some MSi_2-Type Silicides

K. Kurokawa, H. Matsuoka and T. Nagai

Trans. Mat. Res. Soc. Jpn (Elsevier),
Vol. 14 A, 255-258 (1994).

In order to determine oxidation properties of refractory-metal silicides, oxidation tests of $MoSi_2$, WSi_2, $NbSi_2$, and $TaSi_2$ were carried out. In the isothermal oxidation behaviors at 1773 K determined by applying an extremely rapid heating procedure, the weight changes of $MoSi_2$ and WSi_2 were negligibly small as a result of the formation of a glass-like protective SiO_2 layer. On the other hand, such protective oxide layer was not formed on $NbSi_2$ and $TaSi_2$. In addition, the oxidation behaviors of the silicides during heating at a relatively slow rate to 1473 K were also determined. When this heating procedure was applied, a pronounced increase in weight was observed in the silicides except for $MoSi_2$. Furthermore, the effect of the dissolution of WSi_2 upon the oxidation behavior of $MoSi_2$ is discussed. (English)

High Temperature Oxidation Behavior of Structural Silicides

C. E. Ramberg, P. Beatrice, K. Kurokawa
and W. L. Worrell

Mat. Res. Soc. Symp. Proc., Vol. 322, 243-253 (1994).

The factors which control the formation of a protective silica (SiO_2) layer on structural silicides at high temperature are summarized. The thermodynamic and kinetic conditions under which both silica and a metal oxide can form are also described. Molybdenum disilicide ($MoSi_2$) forms highly protective silica scales and has the best oxidation resistance at high temperatures. Although the preparation method has little influence, the heating rate and the structure of the silica layer have significant effects on the oxidation behavior of $MoSi_2$. (English)

Corrosion of Iron and Migration of Corrosion Products in Compacted Bentonite

T. Kozaki, Y. Imamura, J. Takada, S. Sato
and H. Ohashi

Abstracts of Scientific Basis for Nuclear Waste
Management XVIII, 231-232 (1994).

For safety of the geological disposal of the high level radioactive waste, it is necessary to study corrosion of the overpack materials and migration of the corrosion products in the compacted bentonite. In the present study, average corrosion rates of iron foil and apparent diffusion coefficients of the corrosion products were determined using a neutron-activated iron foil. The average corrosion rates were nearly 10^{-6} m/y, while apparent diffusion coefficients were in the range from 10^{-12} to 10^{-14} m^2/s. No tendency to decrease in the corrosion rates with increasing corrosion time were observed. This suggests that the iron foil corrode under reducing condition. Asymmetric concentration profiles of iron corrosion products were obtained in some experiments. It can be considered that either cathodic or anodic reaction would dominantly occur on one side of the iron foil surfaces and that each reaction would change the pH in pore water of bentonite specimens by the iron foil surfaces. (English)

Thermodynamic Properties of Water in Compacted Bentonite under External Pressure-Free Condition

Y. Torikai, S. Sato and H. Ohashi

Abstracts of Scientific Basis for Nuclear Waste
Management XVIII, 41-42 (1994).

In an attempt to determine the thermodynamic properties of water in bentonite, the vapor pressure of water in compacted bentonite was measured as a function of water content and temperature, under external pressure-free condition. The relative partial molar Gibbs free energy ΔG_{H2O}, enthalpy ΔH_{H2O} and entropy ΔS_{H2O} of the water in bentonite were determined at temperature of 298.15 K. The interlayer distance of montmorillonite in bentonite was also measured by X-ray diffraction.

It is probable that one fourth of the total water included in the bentonite at water content of 20.3wt% and dry density of 1.76×10^3 kg/m^3 is free water; the water is not regarded as dilute electrolytic solution, but the solution with higher ionic strength. Another one fourth of the water in the bentonite at the water content is bound water; the partial molar entropy of the bound water referred to pure water is from a half to whole of solidification entropy of pure water. The remainder is regarded as intermediately bound water. (English)

Influence of Humic Acid on Sorption of Neptunium (V) onto Soil

Y. Sakamoto, S. Nagao, T. Ohnuki, M. Senoo,
A. Ohashi, S. Sato and H. Ohashi

Abstracts of Scientific Basis for Nuclear Waste
Management XVIII, 157–158 (1994).

The pH dependence of the stability constant of Np(V)-humate and the sorption of Np(V) onto soil were studied to clarify the influence of dissolved organic carbon on the migration behavior of Np(V) in soil layer. The stability constant of Np(V)-humate was expressed by $\log \beta_1 = (0.35 \pm 0.03)\mathrm{pH} + 0.04 \pm 0.01$ in the pH region from 5.3 to 8.7, and the intrinsic stability constant by $\log \beta_1 = 3.66 \pm 0.05$.

The sorption of Np(V) increased with pH up to pH 7, and tended to reach maximum, about 95%, at pH 9 in the absence of humic acid. In the presnce of humic acid more than 140 mg/l, the sorption of Np(V) was lower than that without humic acid above pH 7, while any influence of humic acid on the sorption of Np(V) onto soil was not observed below pH 7. The sorption behavior of Np(V) onto soil was explained by reversible sorption of NpO^{2+} and sorption of $NpO_2CO_3^-$ and/or NpO_2OH. Further, the influence of the size distribution of Np(V) on the sorption onto soil was examined and discussed. (English)

Cold Fusion may Dissolve the Energy Problems

T. Mizuno

Refrigeration Vol. 69, No. 795, (1994).

Cold Fusion reaction is still discussing obtaining mechanism and controlling. Recently, many positive results have been shown by the possible existence of the reaction as heat generation, ^{4}He particle emission, tritium evolution, high energy charged particle emission and low rate of neutron evolution. However, the entire pictures of it are still in mystery. Very recently, another type of material such as tungsten bronze and $BaTiO_3$ styles of perovskite are used for the candidate of Cold Fusion reactor medium for hydrogen isotopes. If the Cold Fusion can be realized, the system may be composed as mentioned and the convenient materials; the system can be established near the area of demand. The reactor may supply the electric power as the nuclear reactor without any type of radioactive materials and radiations. (English)

Electrochemical Kinetics and Mechanism of Hydrogen Absorption of Ti and Zr During Cathodic Electrolysis

T. Mizuno and M. Enyo

Memoirs of Faculty of Engineering, Hokkaido University,
Vol. XVIII, No. 4 (No. 81) February, 1994.

Relationships between kinetics of hydrogen absorption by eletrolysis and hydrogen concentration profiles of Ti and Zr were investigated by a nuclear chemical and other conventional techniques. Hydrogen atoms interact very intensively with others in the metal. Hydrogen concentration profiles were dependent on the condition of cathodic electrolysis and pre-treatment of metal. 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. (English)

Incorporation of Impurity Metal Ions in Electrolytic Manganese Dioxide

Hiroki Tamura, Kenji Ishizeki, Masaichi Nagayama
and Ryusaburo Furuichi

J. Electrochem. Soc., **141**, [8], 2035-2040 (1994).

The amounts of impurity metal ions incorporated into electrolytic manganese dioxide (EMD) during its preparation were measured as a function of metal ion concentrations and current densities. The amount of incorporated ions increased in proportion to the concentration in solution, and at a fixed concentration it was different from ion to ion: $Ni^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} < Fe^{3+} < Pb^{2+}$. The specific surface area of the formed EMD was larger for impurity ions with higher incorporation affinity. Further, the adsorption of ions on the surface of a ready-made manganese dioxide sample (IC12) was examined, and modeling of the adsorption behavior was attempted. The amounts of adsorbed ions at a fixed concentration in solution and pH 0.7 (where EMD is produced) were obtained by the ion-adsorption model. There was a strong correlation between the amount incorporated and the amount of adsorption, suggesting a mechanism in which EMD is contaminated through adsorption on its new growing surface. The increase in specific surface area of EMD with contaminants was interpreted to be due to a suppression of the growth of EMD at the adsorbed foreign ion sites, resulting in EMD with many defects or smaller particle sizes. The opposite effect of current density on incorporation for the two groups of metal ions was discussed. (English)

Modeling the Ion-Exchange Adsorption of Cobalt (II) Ions on the Surface of Manganese Dioxide Particles

Noriaki Katayama, Seiichi Tamura, Hiroki Tamura
and Ryusaburo Furuichi

Denki Kagaku, **62**, [3], 251-256 (1994).

The ion-exchange adsorption of cobalt (II) ions on manganese dioxide (MnO_2) was modeled to enable description and prediction of the amount of adsorption as a function of ion concentration, exchange site density, and solution pH. The model assumes that Co(II) ions are adsorbed through (1 : 1) and (1 : 2) ion exchange reactions with the protons of acid-type surface hydroxyl groups on MnO_2 ($\equiv$MnOH(a)), and that each exchange reaction is suppressed steadily with the progress of ion exchange due to electrostatic lateral interactions between the species in the solid/solution interphase. The equilibrium conditions of the (1 : 1) and (1 : 2) ion-exchage reactions are given by :

$$K_1^\circ = K_1 \exp(B_1\theta_1) \text{ and } \beta_2^\circ = \beta_2 \exp(B_2\theta_2)$$

where K_1° and β_2° are the equilibrium constants, K_1 and β_2 the concentration ratios, B_1 and B_2 the suppression constants, and θ_1 and θ_2 the coverages of exchange sites. The values of K_1°, β_2°, B_1, and B_2 were determined by fitting the equilibrium-condition equations together with the mass-balance equation for the adsorption sites to the experimental data. The results are: $K_1^\circ = 4.79 \times 10^{-5}$ $mol^{-1}\,m^3$, $\beta_2^\circ = 3.02 \times 10^2\,m^{-1}$, $B_1 = 12.0$, $B_2 = 46.8$ at an ionic strength of 0.1 mol dm^{-3}($NaNO_3$) and 25°C. Based on the model the fraction of adsorbed Co (II) was calculated as a function of pH for fixed concentrations of added Co (II) and MnO_2. The calculated fraction was compared with those of Cu (II) and Zn (II) obtained for the same conditions. The affinity of Co (II) for MnO_2 is about the same as Zn (II), but far smaller than Cu (II). (Japanese)

Modeling of Divalent Heavy Metal Ion Adsorption on the Surface of Iron(III) Oxide Particles

Hiroki Tamura, Koji Okita, Noriaki Katayama
and Ryusaburo Furuichi

Bunseki Kagaku, **43**, [11], 831-836 (1994).

Soils and sediments contain metal oxide particles and control the concentration of heavy metal ions in natural waters at low levels by adsorption. The adsorption isotherms of divalent heavy metal ions on the surface of iron(III) oxide particles were obtained, and modeling of the adsorption reaction was made to describe and predict water quality. The model assumes (1) surface complex formation due to the (1 : 1) and (1 : 2) cation exchange reactions with protons of acid surface hydroxyl sites and (2) suppression of the reactions by a linear increase in the Gibbs free energy change (ΔG) with the surface coverage. From the model parameters, it was found that the adsorption affinity increases in the order: $Co^{2+} \leq Zn^{2+} < Cu^{2+} < Pb^{2+}$. There was a good correlation between the stabilities of surface complexes and hydroxo complexes for these ions. This supports the surface complexation model which assumes that metal ion adsorption is due to the donation of electron pairs from the lattice oxide ions to the metal ion. (Japanese)

X-Ray Photoelectron Spectroscopic Study of Hydrated Aluminas and Aluminas

Takeshi Tsuchida and Hideaki Takahashi

J. Mater. Res., **9**, 2919–2924 (1994).

X-ray photoelectron spectra of hydrated aluminas (boehmite, diaspore, bayerite, and gibbsite), transition aluminas (γ, δ, η, θ, χ, and κ-Al_2O_3) and corundum (α-Al_2O_3) have been studied for spectral characterization of each compound. The O 1s spectra shifted 0.2–1.2 eV to higher binding energy (E_b) in the order of α-$Al_2O_3 <$ boehmite, diaspore $<$ bayerite, gibbsite, and this agrees with the order of bulk OH/Al molar ratio in samples. The E_b and FWHM values of O 1s spectra of transition aluminas depend on the ratio OH/O, i.e., the amount of OH^- ions chemisorbed on them, and tend to decrease toward those of α-Al_2O_3 with increasing calcination temperature. Therefore, it is considered that an attracting effect of the proton on valence electrons in the hydroxyl oxygen causes the increased binding energy between core electrons and oxygen atomic nuclei. The broad O 1s spectra of boehmite and diaspore can be deconvoluted into equal contribution the two oxygen species in O^{2-} and OH^- ions in their structures. (English)

Electroluminescence from p-Type Silicon during Anodic Oxidation in Ethylene Glycol Solution

M. Seo, K. Fushimi, H. Takahashi and K. Aotsuka

J. Electroanal. Chem., **368**, 257-264 (1994).

Electroluminescence (EL) from p-type Si during anodic oxidation under galvanostatic conditions in ethylene glycol solutions of KNO_3 with and without different concentrations of chloride ions was measured to investigate the relation between the EL behavior and the defective structure of the silica film formed on Si by anodic oxidation. The measured broad EL spectra had two peaks at 370 nm and 670 nm. The EL peak intensity of the 670 nm peak, rather than that of the 370 nm peak, was enhanced significantly by the addition of chloride ions to the solution, from which it is deduced that the EL source of 670 nm is associated with point defects which are increased by the incorporation of chloride ions in the film. Comparison between the film thickness measured with ellipsometry and the total electric charge required for anodic oxidation revealed that the current efficiency for film growth is only 1% and the majority of the anodic current is electronic, due to electrons injected into the conduction band of the silica film from solution. The relation between EL peak intensities and electrode potential suggested that the EL is operative in an impact ionization-electron avalanche mechanism, where electrons accelerated by a high electric field (2×10^7 V cm^{-1}) in the film come into collision with the EL source. The origin of the EL peaks of 670 nm and 370 nm is discussed on the basis of the EL mechanism using an electronic band model of the Si/SiO_2/solution system. The breakdown of the silica film due to chloride ions was accompanied by abrupt decreases in the EL peak intensities as well as a rapid potential drop, indicating that EL can be used to monitor breakdown of the film. (English)

Quartz Crystal Microbalance

Masahiro Seo

J. Surf. Finish. Soc. Japan, **45**, 1003-1008 (1994).

Quartz crystal microbalance (QCM) technique is capable of detecting small mass changes in the region of nanograms per square centimeter from resonant frequency changes of the quartz crystal.

In this article, the principle and measurement method of QCM were described and the typical examples of experimental results obtained by application of QCM to atmospheric and aquous corrosion of metal thin films were introduced. Moreover, the problems of application of QCM were pointed out and discussed. (Japanese)

A Combined Piezoelectric and EQCM Study of Underpotential Deposition of Silver on Gold Electrodes

Masahiro Seo, Masaki Aomi and Kengo Yoshida

Electrochim. Acta, **39**, 1039–1044 (1994).

The piezoelectric detection of change in surface energy combined with the use of electrochemical quartz crystal microbalance (EQCM) was applied to underpotential deposition (*upd*) of silver on gold electrode. The *upd* of silver on gold was performed with a potentiodynamic method (10 $\mathrm{mVs^{-1}}$) in a deaerated solution of 0.1 $\mathrm{mol\ dm^{-3}\ Na_2SO_4 + 10^{-3}\ mol\ dm^{-3}\ H_2SO_4 + 5\times10^{-5}\ mol\ dm^{-3}\ Ag_2SO_4}$.

The amplitude, $|A|$, and phase angle, ϕ, of the piezoelectric signals changed depending on the adsorbed amount of silver in the potential range of 1.10–0.56 V (*she*). Particularly, two characteristic potentials at which $|A|$ took a minimum value and ϕ changed by about 140°, appeared in both anodic and cathodic potential sweep. The characteristic potentials, $E=0.62$ V, and $E_2=0.90$ V (*she*) correspond to the potentials of electrocapillary minimum and maximum, respectively. The presence of two characteristic potentials during the *upd* was explained by taking into account the changes in adsorption state of $\mathrm{HSO_4^-}$ or $\mathrm{SO_4^{2-}}$ ions. The EQCM results indicated that the complete charge transfer of silver ions, $z=1$ takes place during the *upd*. The piezoelectric detection of change in surface energy responded sensitively to the structural changes in the *upd* adsorbate as compared with the EQCM. (English)

Structural Strain in Pyrites Evaluated by X-Ray Powder Diffraction

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Two parameters for measuring the structural strain, the effective Debye-Waller parameter, B_{eff}, and lattice strain, ε, were evaluated on a natural pyrite (FeS_2) after grinding. The effective Debye-Waller parameter, B_{eff}, which depends on the displacement of atoms in the crystal, was calculated for the overall crystal, B_{eff} (FeS_2), and for sulphur, B_{eff}(S), from the intensities of the X-ray diffraction lines. The B_{eff}(S) increased markedly with increasing grinding time, while B_{eff}(FeS_2) did not change significantly. The lattice strain, ε, was not recognized. These observations suggest that the displacement of sulphur atoms preferentially takes place by grinding. The relations between these B_{eff} values and crystallite size, L, were observed to be common for two different methods of grinding. This tendency was considered to be an inherent property of pyrite. The value of B_{eff}(S) is a useful index to estimate mechanically caused strain in pyrite. (English)