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ELECTROCHEMISTRY LABORATORY

Prof. Dr. M. Seo, Assoc. Prof. Dr. H. Takahashi,
Dr. K. Azumi, Dr. K. Noda and Miss J. Fujiwara

Students

M. Aomi, K. Fujiwara, K. Yoshida, M. Dairaku, K. Shigyou,
K. Nukui and S. Watanabe

Prof. M. Seo attended the 12th Scandinavian Corrosion Congress & Eurocorr '92 which was held in Dipoli, Espoo, Finland on May 31–June 4, 1992 and presented a paper entitled "Study on Anodic Deposition of Ferrous Ions on Gold in Aqueous Solutions Containing Chloride Ions by a Quartz Crystal Microbalance". Afterward, Prof. M. Seo visited Professor C. Leygraf and Dr. G. Hultquist at Royal Institute of Technology, Stockholm, Sweden and Professor I. Olefjord at Chalmers University of Technology, Goteborg, Sweden on June 5–June 19 for Collaborative Study on Minute Corrosion of Metal Thin Films which was supported by Japan Society for The Promotion of Science and Royal Swedish Academy of Science.

Dr. H. Takahashi was invited to give a lecture on "The Recent Investigation on Anodizing of Aluminum and Its Alloys" at the 2nd Seminar on Corrosion and Protection, which was held at Bangkok, Thailand under the sponsorship of Japan International Cooperation Agency (JICA) on June 30–July 2.

Dr. Kazuhiko Noda joined our laboratory as a research associate on August 1st. Dr. Kazuhisa Azumi left for Department of Materials and Engineering, Stanford University, California, U.S.A. to conduct the electrochemical study of solid electrolytes for fuel cells with Professor D. A. Stevenson for one year.

Professor M. Seo visited Bangkok, Thailand on September 28–October 6 to present the Lectures on Fundamental Electrochemistry of Metallic Corrosion at Thailand Institute of Science and Technological Research, Chulalongkorn University, and King Mongkuts Institute of Technology Thonburi, which was supported by the Project on Atmospheric Corrosion-Organic Coating of Japan-Asean Cooperation on Science and Technology.

On October 6–17, Dr. H. Takahashi visited U.S.A. and Canada. He discussed with Prof. W. H. Smyrl, Prof. R. A. Oriani, Prof. R. Staehle, Prof. H. S. White, and Prof. M. D. Ward at Corrosion Research Center, University of Minnesota, and with Prof. K. Hebert. at Iowa State University. In Canada he attended the 182nd Annual Meeting of the Electrochemical Society at Toronto, and presented a paper on "The Films Formed on Aluminum by Duplex Thermal/Anodic Oxidation Processes".

The following scientists visited this laboratory : Dr. J. Manassen, Weizman Inst. of Sci., Israel, on Apr. 14, Prof. S. Mrovec, Academy of Mining and Metallurgy, Poland, on May 15, Ms. N. Thanuddhanusilanp Thailand Inst. of Sci. and Tech. Res., Ms. L. A. de Guzman, Industrial Tech. Devp. Inst., Philippines, and Ms. S. Nurdiati, Res. and Devp. Center for Metallurgy, Indonesia, on June 2–3, Prof. Z. Jiang, Fudan Univ., China, on June 16–21, Dr. D. Meissner, Dept. of Photoelectrochem. and New Mat., on Nov. 30, and Ms. N. Chulasai, Metal and Mat. Tech. Dept., Thailand, Ms. W. Rungruyankanokkul, Metallurgy and Mat. Sci. Res. Inst., Thailand, Ms. R. G. Principe, and Ms. E. L. Enriquez, Industrial Tech. Devp. Inst., Philippines, on December 7–9.

The research activity of the laboratory still continues to be directed towards a better undersanding 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 Underpotential Deposition of Pb and Ag on Au Electrode*

The underpotential deposition (UPD) of Pb and Ag on Au electrode in perchlorate and sulphate solutions has been investigated from the piezoelectric response of surface stress change induced by a potential modulation. The UPD of Pb shifts the potential of zero charge (pzc) of Au to the noble direction by about 0.2 V.

On the other hand, the sign reversal of surface charge of Au takes place twice during UDP of Ag, which is ascribed to the different adsorption states of sulphate ions depending on the surface coverage of Ag.

(2) *Corrosion and Passivation of Iron Thin Films by QCM*

A quartz crystal microbalance (QCM) technique was applied to investigate the corrosion and passivation of iron thin films in deaerated pH 6.48 boric-borate solution. The iron thin films were electroplated on gold electrode of quartz oscillator from $FeSO_4$ $(NH_4)_2SO_4 \cdot 6H_2O$ solution.

The QCM results indicated that the significant dissolution of iron preceded the formation of the passive film, and that the predominant process of passivation was the anodic deposition of ferrous ions once dissolved. The anodic current of iron dissolution and cathodic current of hydrogen evolution could be separately obtained as a function of electrode potential from the mass change of iron thin films measured during galvanostatic polarization near the corrosion potential.

(3) *Photoelectrochemistry of TiN Thin Films*

TiN thin films (2 μm) were deposited on Pt or SUS 304 stainless steel substrates by a cathodic arc ion plating method. The TiN films on the substrates were anodically polarized in deaerated pH 8.4 boric-borate solution. The photocurrent of the TiN film during anodic polarization was measured under the illumination of polychromate light from a 500 W xenon lamp.

The photocurrent was anodic and increased with increasing anodic potential, indicating a n-type semiconductive properties. The formation of TiO_2 surface film during anodic polarization of TiN was confirmed with FT-IR analysis. The anodic photocurrent, therfore, is ascribed to the formation of TiO_2 surface film with n-type semiconductive properties.

(4) *Cathodic Polarization of Aluminum Covered with Anodic Oxide Films*

Cathodic polarization behavior of aluminum covered with porous type- and barrier type-anodic oxide films has been examined by potential sweep method in a neutral borate solution. During cathodic polarization, the dissolution of the metal substrate took place to form many pits. The number of pits formed on porous type-oxide films was larger than that on barrier type-oxide films. The specimen subjected to the chemical dissolution in an acid solution prior to the cathodic polarization exhibited the formation of a large number of pits, suggesting the significance of film imperfections in the pit formation.

(5) *Anodizing of Aluminum with Laser Irradiation*

Anodizing of aluminum has been investigated under the irradiation with YAG-laser. Porous type-anodic oxide films were found to be formed only at the position irradiated with laser by covering with barrier type-anodic oxide films before anodizing. The film formation rate during anodizing with laser irradiation was lower than that during conventional anodizing. Electron microscopic observation showed the pore-branching in the oxide films.

(6) *Anodic Oxidation of Aluminum Covered with Thermal Oxide Films*

Aluminum covered with thermal oxide films was anodized galvanostatically in a neutral borate solution at different temperatures between $T_a = 293$ and 353 K to examine the formation of barrier-type anodic oxide films. The rate of increase in the anode potential showed a maximum at 323 K and the current efficiency for film formation decreased with increasing temperature. Electron microscopy showed that the anodic oxide films formed at all T_as below 353 K have a sandwich structure of amorphous oxide-, crystalline oxide-, and amorphous oxide-layers, and that the thickness of the crystalline oxide layer increases with increasing T_a. The anodic oxide film formed at 353 K was composed of a single layer of crystalline oxide.

Oral Presentation

Acoustic Emission from Palladium during Electrochemical Hydrogen Absorption; S. Ishiguro, K. Azumi, T. Mizuno and M. Seo: The 18th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan., 1992

Electroluminescence from Metals Subjected to Aodic Oxidation in Ethylene Glycol Solution; K. Fushimi, K. Azumi, H. Takahashi and M. Seo: *ibid.*, Jan., 1992

Application of QCM to Minute Corrosion of Thin Film Material and Its Problem; M. Seo: The 1st Hokkaido Section Meeting of Jpn. Soc. Corros. Eng., Jan., 1992

Formation of Crystalline Anodic Oxide Films on Aluminum by Duplex Processes of Thermal and Anodic Oxidation; C. Ikegami, H. Takahashi and M. Seo: *ibid.*, Jan., 1992

Structure of Anodic Oxide Films Formed on Aluminum by Thermal and Anodic Oxidations; C. Ikegami, H. Takahashi and M. Seo: The 1992 Winter Meeting of The Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., Feb., 1992

Imperfections in Anodic Oxide Films Formed on Aluminum by Thermal and Anodic Oxidations; C. Ikegami, H. Takahashi and M. Seo: The 85th Annual Meeting of Metal Finishing Soc. Jpn., March, 1992

Pursuit of Anodic Deposition Process of Ferrous Ions on Gold Electrode by QCM; M. Seo and K. Yoshida: The 59th Annual Meeting of Electrochem. Soc. Jpn., Apr., 1992

Electrochemical Measurements of Diffusion of Hydrogen and Deuterium in Palladium; K. Azumi, T. Fujita, T, Ito, T. Mizuno and M. Seo: *ibid.*, Apr., 1992

Acoustic Emission from Palladium during Absorption Processes of Hydrogen; K. Azumi, S. Ishiguro, T. Mizuno and M. Seo; *ibid.*, Apr., 1992

Effects of Stress and Potential on the Corrosion Fatigue of SiC-Reinforced Aluminum; K. Noda and T. Tsuru: The 1992 Spring Meeting of Jpn. Inst. of Matals, Apr., 1992

Stress Corrosion Cracking of SiC-Reinforced Aluminum. —Effect of Orientation of SiC Whisker—; H. Ono, K. Noda and T.

Tsuru: *ibid.*, Apr., 1992

Membrane Potential of Ni-Hydroxide; M. Seo, Y. Furukawa and I. Ninomiya: '92 Spring Meeting of the Jpn. Soc. Corros. Eng., May, 1992

Impedance Measurements during Anodic Polarization of Titanium Covered with Passive Oxide Films; K. Azumi and M. Seo: *ibid.*, May, 1992

Time Variation in The Current during The Corrosion Fatigue of SiC-Reinforced Aluminum; K. Noda and T. Tsuru: *ibid.*, May, 1992

Introduction of Anodic Oxidation; H. Takahashi: Seminar on Metal Finishing for Beginners, June, 1992

Study on Anodic Deposition of Ferrous Ions on Gold in Aqueous Solutions Containing Chloride Ions by a Quartz Crystal Microbalance; M. Seo and Y. Yoshida: The 12th Scandinavian Corros. Cong. and Eurocorr '92, Espoo, Finland, June, 1992

Recent Investigation on Anodizing of Aluminum and its Alloys; H. Takahashi: The 2nd Seminar on Corrosion and Protection (Sponsored by Acean-Japan Corporation on Mat. Sci. and Tech., Bangkok, Thailand, June, 1992

QCM Study on The Anodic Deposition of Ferrous Ions And on The Cathodic Reduction on The Deposited Film; K. Yoshida and M. Seo: The 1992 Summer Meeting of The Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., July, 1992

Rectification Phenomena on Aluminum Covered with Porous- and Barrier-Type Anodic Oxide Films; K. Fujiwara and H. Takahashi and M. Seo: *ibid.*, July, 1992

QCM Study on The Cathodic Reduction Process of Ferric hydroxyoxide Film; M. Seo and K. Yoshida: '92 Fall Meeting of Electrochem. Soc. Jpn., Sept., 1992

ICP-Atomic Emission Spectroscopic Study on Anodizing of ADC 12 Aluminum Die-Casting Alloys; H. Takahashi, K. Shiga and M. Seo: *ibid.*, Sept., 1992

Anodic Oxidation of Aluminum Covered with Thermal Oxide

Films; H. Takahashi: Symp. on Surf. Modification of Aluminum, Sept., 1992

Effects of Potential on the Stress Corrosion Cracking of 8090-Al/Li Alloy; E. Tada, K. Noda, T. Tsuru, T. Hagiwara and K. Kobayashi: The 1992 Fall Meeting of Jpn. Inst. of Metals, Oct., 1992

Cathodic Polarization Behavior of Aluminum Covered with Porous and Barrier Type Oxide Films; H. Takahashi, K. Fujiwara, K. Kasahara and M. Seo: Seminar at Iowa State Univ., Ames U.S.A., Oct., 1992

Oxide Films Formed on Aluminum by Duplex Thermal/Anodic Oxidation Processes. —Effect of Pretreatment—; H. Takahashi, C. Ikegami and M. Seo: Symp. on Oxide Films on Metals and Alloys (The 182nd Meeting of Electrochem. Soc., Toronto, Canada), Oct., 1992

Piezoelectric Response to The Under-Potential Deposition of Lead on Gold Electrode; M. Aomi and M. Seo: The 86th Annual Meeting of Metal Finishing Soc. Jpn., Oct., 1992

QCM Study on Formation and Cathodic Reduction Processes of Iron Passive Films; K. Yoshida and M. Seo: The 39th Symp. on Corrosion and Protection, Oct., 1992

Breakdown of Aluminum Anodic Oxide Films by Cathodic Polarization; K. Fujiwara and H. Takahashi and M. Seo: *ibid.*, Oct., 1992

Electroluminescence from p-Type Silicon during Anodic Oxidation; K. Fushimi and M. Seo: Seminar on New Material for Harmful Gas Capturing, Nov., 1992

Effects of Anion Incorporation on The Properties of Aluminum Anodic Oxide Films; H. Takahashi: The 9th ARS Azumino Conference (Sponsored by Metal Finishing Soc. Jpn.), Nov., 1992

NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. H. Ohashi, Assoc. Prof. Dr. S. Sato,
Dr. T. Mizuno, Mr. T. Kozaki, Mr. K. Hirohara
and Miss R. Oyama

Students

Y. Tasiro, T. Fukuda, Mohamad Samadfam, Y. Imamura,
A. Ohashi and Y. Miyazaki

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 nobel metal fission products in UO_2, and radioactive waste management.

(1) Hydrogen storage alloys, i.e., La-Ni or Mm-Ni were tested in an aqueous solution as the electrode of a fuel cell. Several types of alloy system were examined in various conditions. All alloys were first activated and pulverized to small particle, and they were mechanically compressed, and were sintered. The specimens obtained were examined stability in the electrolyte, disintegration during charge-discharge cycles. The sintered and activated La-Ni alloy is a promising electrode for the hydrogen storage type fuel cell.

(2) Passivation and Pitting of stainless steel was studied by a spectrum analysis of fluctuation of the corrosion currents. The shape of the spectra is expressed by the $f^n(-1 \leqq n \leqq 0)$ relationship in the range of frequency from 10^{-2} to 10Hz. The method is applied for, first, estimation of the stability of a passive film in a neutral solution and, then, prediction of the pit generation.

In the passivation process, spactra change with increase in the thickness of film, and slope, n, approaches to zero. After the addition of Cl^- ions, n is nearly zero, while the passive film is stable. However, the change in n appeared, $(-1 \leqq n \leqq 0.5)$, when the film became unstable, and sporadic tiny pits are 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 the Pd on the fuel performance, the migration behavior of the Pd in uranium dioxide pellet has been studied. Penetration profiles of the Pd in the pellet were obtained by an electron probe mocro-analysis. Diffusion coefficients of Pd 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, an evaluation of several migration processes are under way.

(4) The corrosion behavior of iron and the migration behavior of some metal ions in bentonite were studied to assess the performance of an engineered barrier in geological disposals of radioactive wastes. Apparent diffusion coefficients of metal ions in the bentonite were determined, using radioactive tracers (Fe-59, Cr-51, Co-60 and Mn-54).

(5) In basic reseach of bentonite, the vapor pressure of water in bentonite was measured as a function of temperature and water content. The enthalpy and the entropy of water in the bentonite were obtained from the temperature dependence of the vapor pressure. The condition of free water in the bentonite is discussed on the basis of the thermodynamic data as well as the interlayer distance obtained by the XRD method.

(6) For purposes of safety analysis of nuclear waste disposal, the migration processes of fission products and actinides in geologic formation has to be clarified. One of the processes, where study is very limited, is that involving humic acid and fulvic acid. Sorption coefficients of Sr on powder of granitic rock were measured by a batch method, using Sr-85 as a radiotracer, as a function of contact time, pH, Sr-concentration and concentration of humic acid.

Oral Presentation

Observation of Corrosion by Spectrum Analysis of Current Fluctuation ; Febriant, T. Mizuno and H. Ohashi : The First Annual Meeting of Hokkaido Section of Japanese Society of Corrosion Engineering, Jan, 17. Sapporo. 1992.

Confirmation of the Fleishmann-Pons Effect (Cold Fusion); T. Mizuno: The International Symposium on Nonlinear Phenomena in Electromagnetic Fields, Nagoya, Jan., 26-29, 1992.

Migration Behavior Palladium in UO_2 (II); M. Yoneyama, S. Sato, H. Ohashi, T, Ogawa, A. Ito and K. Fukuda: Annual Meeting of Atomic Energy Society of Japan, March, 1992.

Acoustic Emission from a Palladium Electrode During Hydrogen Charging; K. Azumi, S. Ishiguro, T. Mizuno and S. Seo: The 59th Annual Meeting of Electrochem. Soc. Japan, Apr., 2., 1992.

Electrochemical Study of Diffusion of Hydrogen and Deuterium in Palladium; K. Azumi, T. Fujita, T. Ito, T. Mizuno and S. Seo: The 59th Annual Meeting of Electrochem. Soc. Japan, Apr., 2., 1992.

The Relationship between Behavior of Deuterium in Palladium and Cold Fusion; T. Mizuno, T. Akimoto, K. Azumi and M. Enyo: The First West Pacific Electrochemistry Symposium, May, 25-27, 1992.

Stability Constants and Structures of Uranyl and Thorium Chloro-Complexes; H. Ohashi and T. Morozumi: Rare Earths, '92 in Kyoto, June, 1-5, 1992.

Thermodynamic Properties of Water in Compacted Bentonite; S. Sato, N. Taniguchi, T. Kozaki and H. Ohashi: Fall Meeting of Atomic Energy Society of Japan, Oct., 1992.

Diffusion Behavior of Fe in Compacted Bentonite (II); H. Kato, T. Kozaki, S. Sato, H. Ohashi, T. Tamai, J. Takada, T. Ohe and M. Tsukamoto: Fall Meeting of Atomic Energy Society of Japan, Oct., 1992,

Effects of Humic Acid on Sorption of Sr on Granitic Rock; H. Ohashi, M. Honda, J. Arisawa and S. Sato: Fall Meeting of Atomic Energy Society of Japan, Oct., 1992.

Cold Fusion Reaction Products and Behaviour of Deuterium Absorption in Pd Electrode; T. Mizuno, T. Akimoto, K. Azumi and M. Enyo: The Third International Conference on Cold Fusion, Nagoya Congress Center, Nagoya, Japan, Oct., 1992.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Prof. Dr. H. Tamura,
Lecturer Dr. H. Konno, Mr. I. Saeki
and Miss. R. Hashimoto

Students

A. Furusaki, K. Ishizeki, M. Watanabe, A. Uchibo, K. Ohkita,
R. Hata, T. Miyai, H. Okudera and N. Kikuchi

Dr. Konno was invited by JICA to Seminar/Workshop on Corrosion of Metals for ASEAN-Japan Cooperation on Materials Science and Technology held in Manila, Philippines, in June. He also joined International Conference on Advances in Corrosion and Protection held at The Corrosion Centre of UMIST in Manchester, U.K., in June-July. Dr. Tamura jointed The Tianjin International Power Sources Symposium held at Tianjin, China, in September.

The research programs in our laboratory are:

(1) *Preparation of Mn spinel oxide and characterization of its ion exchange properties, very specific to Li ions*

Lithium-manganese spinel oxide was prepared by thermal reaction between Li_2CO_3 and Mn_2O_3, and lattice Li ions were removed by washing with HNO_3 solution. The spinel structure was retained. even after the Li sites became vacant. This oxide reincorporates Li ions selectively in the vacant (originally Li) sites, and is called "an ion-memory exchanger", considered capable of recovering Li ions from sea water. The crystal structure, chemical composition, and specific surface area were studied, and the behavior of adsorption of Li ions is being examined as a function of Li ion concentration and pH.

(2) *Modeling ion-exchange reactions*

Modeling ion exchange adsorption of ions by metal oxides and organic solids was conducted to describe and predict the extent of adsorption. The models assume that apparently one ion exchange reaction is composed of several parallel reactions with different reactivities, and that each exchange reaction is suppressed with the progress of the ion exchange due to electrostatic lateral interactions between the species in the solid/solution interphase. The models can be applied to assessing and simulating the migration of hazardous ions in the groung from underground waste repositories.

(3) *Purification of Mn(II) sulfate electrolyte solution for MnO_2 preparation*

Manganese dioxide for battery purpose is produced by electrolysis of Mn(II) sulfate solutions. The Mn(II) sulfate solutions prepared from Mn ore contain considerable amounts of ions harmful to batteries, and the methods and conditions to remove such ions are being examined.

(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 further developed to form thin oxide films on ceramics and metals. The method utilized ultrasonic spraying and pyrolysis. First, the formation of $LaCrO_3$ and $LaCr_{0.5}Mn_{0.5}O_3$ films were attempted. The formation rate of films was found to depend on spraying time and substrate temperature. As deposited films showed certain type of XRD patterns but so far they are not identified. The deposited films were converted to perovskite oxides by the pyrolysis at 800°C for 15 min in nitrogen. Further investigations are in progress.

(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, in which cathodic reduction of nitrate ions was used to control the surface pH. The Al(III)-Y(III) mixed hydroxide films having Y(III) content up to 60% were formed on nickel or stainless steels. It was found, however, that high content of Y(III) in the films cannot be explained by simple precipitation equilibrium of hydroxides. Further investigation on the deposition mechanism is in progress. After drying at 350°C, the films showed good performance as protective oxide coatings under oxidizing atmosphere at elevated temperatures.

(6) *Formation of Nitride/Oxide Mixed Films on Titanium via Anodizing*

As reported previously, it is possible to form anodic oxide films containing metal-oxinate from aqueous solutions containing oxine (8-hydroxyquinoline). By applying the anodizing technique to titanium followed by pyrolysis in argon atmosphere, nitride/oxide films were formed on a Ti sheet. Further investigations have been started.

(7) *Atmospheric corrosion of SENDUST*

The SENDUST is Fe-Si-Al magnetic alloys which show very high initial permeability around 85Fe-10Si-5Al. The corrosion resistance of the alloys can be impoved by doping a small amount of Nb, Ti, Zr, and so on. In the present work, atmospheric corrosion of undoped and Nb or Ti doped alloys were examined at room temperature by forming very thin water film containing Na_2SO_4 on them. It was found that after the corrosion experiments, the composition of surface films formed on Ti doped alloys are different from others and it may be related to the improved corrosion resistance.

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

The establishment of films on metals and alloys is not well understood because there has been no suitable analytical tools. Thin films grown on Fe-Cr alloys oxidized for 0 to 180 s at 1273 K were analyzed with several methods (TLXRD, XPS, AES-SAM, FTIR-RAS, and FE-SEM) sensitive to surface properties, and a model of the initial oxide formation has been developed. It was found that trace amounts of manganese affect the oxide properties.

Oral Presentation

Codeposition of Impurity Metal Ions in Electrolytic Manganese Dioxide; K. Ishizeki, H. Tamura and R. Furuichi: The 18th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan. 1992.

Analysis of the Exchange Behavior of Li^+, Na^+, K^+ and Cs^+ Ions with Porous Type Ion Exchange Resin; M. Kudo, H. Tamura and R. Furuichi: The 1992 Winter Meeting of the Hokkaido Sections of Jpn. Soc. for Anal. Chem. and Chem. Soc. of Jpn., Feb. 1992.

Effect of Oxygen Partial Pressure on the Formation of $LaCrO_3$ by Pyrolysis; A. Furusaki, H. Konno and R. Furuichi: The 1992 Winter Meeting of the Hokkaido Secs. of Jpn. Soc. Anal. Chem. and Chem. Soc. Jpn., Feb., 1992.

Formation of Aluminium-Yttrium Mixed Oxide Films by Electrodeposition; H. Konno, R. Segawa and R. Furuichi: The 85th Meeting of Surf. Finish. Soc. Jpn., Mar., 1992.

Effect of Grinding on the Surface Chemical States and Solubility of Pyrite; K. Sasaki, M. Tsunekawa, T. Hirajima and H. Konno: The 1992 Annual Spring Meeting of Min. and Mat. Proc. Inst. Jpn., Mar., 1992.

Analytical Chemical Theory of the Activity Coefficients of Adsorbed Ions in the Solid/Solution Interphase; H. Tamura and R. Furuichi: The 63rd Spring Annual Meeting of the Chem. Soc. of Jpn., Mar. 1992.

Initial Oxidation Behavior of the Type 430 Stainless Steel in High Temperature Moist Atmosphere; I. Saeki, H. Konno and R. Furuichi: FUSHOKU-BOSHOKU '92, Apr. 1992.

Electrochemical Formation of Protective Oxide Coatings on Steels to Improve Resistance to High Temperature Oxidation; H. Konno: ASEAN-Japan Cooperation on Materials Science and Technology, Seminar/Workshop on Corrosion of Metals, Manila, Philippines, June, 1992.

Effect of Niobium Doping on the Atmospheric Oxidation of Fe-

Si–Al Magnetic Alloy; H. Konno, S. Matsugi, I. Saeki, R. Furuichi and T. Nishimura: Advances in Corrosion and Protection, Manchester, U.K., June, 1992.

Preparation of High Purity EMD-Uptake of Impurity Metal Ions-; H. Tamura: The 6th Inuyama Conference, Jul. 1992.

Characterization of Ion Exchange Properties of Metal Oxides; H. Tamura: The 7th Ion Exchange Seminar, Jul. 1992.

Affinity of Lithium Ions for Surface Hydroxyl Groups on Manganese Dioxide; TIPSS/TS '92, Sep. 1992.

XPS and Glancing-angle XRD Analyses of the Initial Oxide Films Formed on a Ferritic Stainless Steel; I. Saeki, H. Konno and R. Furuichi: The 86th Meeting of Surf. Finish. Soc. Jpn, Oct., 1992.

Surface Reactions on a Al–Mn Alloy in Solutions Containing Oxidizing Agents; H. Konno, I. Saeki and R. Furuichi: The 86th Meeting of Surf. Finish. Soc. Jpn, Oct., 1992.

Initial Oxidation Behavior of the Type 430 Stainless Steel at High Temperature; I. Saeki, H. Konno and R. Furuichs: The 39th Japan Corrosion Conference, Oct. 1992.

Synthesis of Perovskite Type $La(Cr, Mn)O_3$ by Pyrolysis of Precursors; A. Furusaki, H. Konno and R. Furuichi: Annual Meeting of the Tohoku–Hokkaido Section of Jpn. Ceramics Soc., Nov., 1992.

ELECTROMETALLURGY LABORATORY

Prof. Dr. T. Ishikawa, Assoc. Prof. Dr. T. Sasaki,
Dr. T. Notoya and Mr. S. Konda

Visiting Research Fellow

Assoc. Prof. N. Guo

Students

T. Kumagai, M. Kosaka, M. Noguchi, T. Matsuhashi,
M. Nakata, M. Ueda, K. Kondo, S. Hara,
Y. Nara and T. Suenobu

Professor Ishikawa attended the 8th International Symposium on Molten Salt in St. Louis, U.S.A., in May, and Professr Ishikawa and Mr. Konda participated in the 4th Japan-China Bilateral Conference on Molten Salt Chemistry and Technology, in November.

Dr. Notoya attended the conference to recognize the 20th Anniversary of the Corrosion and Protection Center, UMIST, Manchester, England in June-July. He also participated in the International Symposium on Control of Copper and Copper Alloys Oxidation in Rouen, France in June.

Associate Professor N. Guo from the Institute of Chemical Metallurgy, Beijing, China, stayed from April to November, 1992, to conduct research on plating alloys in low-temperature molten salts.

Researches in progress are as follows.

(1) 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/or $TiCl_4$ in the temperature range from 700 to 800°C.

(2) In order to save, much energy in producing pure aluminum from aluminum scraps, an electrochemical cycle system composed

of three stepwise processes in molten salts was developed and the characteristics of one process of the system, the aluminum chlorine fuel cell, are under study.

(3) Co-deposition reaction of several metals with aluminum in low-temperature chloride molten salts containing $AlCl_3$ is being studied together with investigation of the characteristics of $AlCl_3$–NaCl containing the chlorides of the metals.

(4) A novel galvanic cell for the reduction of the oxygen concentration in tap water in pipe lines was developed and its performance is under investigation.

(5) The corrosion resistance of various kinds of chromium containing alloys in sulfuric acids is being evaluated by electrochemical techniques.

(6) In relation to the corrosion of electronic circuits, electrochemical and spectroscopic investigations on copper and tin-lead alloys are in progress. The corrosion behavior of magnesium alloys containing aluminum also continues to be investigated by electrochemical and spectroscopic methods.

(7) As a model of atmospheric corrosion of metals, surface layers of iron and copper exposed to several kinds of corrosive gas mixtures are being investigated by using in-situ spectroscopic techniques.

(8) Surface tarnishing and its inhibition of copper and copper alloys have been studying with benzotriazole and its derivatives by using electrochemical and surface analytical techniques. Corrosion mechanisms of copper in oils and the preventive measures of cuprosolvency problems in tap water are also being investigated.

(9) Investigations into the in situ spectroelectrochemical phenomena on aromatic thiols adsorbed on the surface of gold by using Fourier transform infrared reflection absorption spectroscopy continue.

Oral Presentation

Dissolution Forms of $TiCl_4$ in High-temperature Chloride Melts; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The

18th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1992.

Reduction in Concentration of Oxygen dissolved in Tap Water by Galvalvanic Cell Reaction; M. Kosaka, S. Konda, T. Sasaki and T. Ishikawa: The First Hokkaido Section Meeting of Japan Society of Corrosion Engineering, Jan., 1992.

Dezincification of Brass; H. Tanaka, S. Konda, T. Sasaki and T. Ishikawa: ibid., 1992

On the Bacteria Corrosion of Copper Tubes; T. Notoya: The 6th Division Meeting of Copper Development Association of Japan, Feb., 1992.

Inhibition of Ant-nest Corrosion of Copper Tubes by Pretreatment with 2-Undecylimidazole; T. Notoya: The 63rd Spring Meeting of Japan Chemical Society, March, 1992.

Prevention of "Ant's-nest Corrosion" in Copper Tubes by Surface Pretreatment; T. Notoya and T. Ishikawa: Corrosion and Corrosion Prevention '92, Apr., 1992.

On the Dissolution of $TiCl_4$ in High-temperature Chloride Melts; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The 59th Annual Meeting of Electrochem. Soc. Japan, Apr., 1992.

Characteristic Analysis of $Al-Cl_2$ Cell in Chloride Melts; M. Maeda, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Apr., 1992.

Reducion in Oxygen dissolved in Tap Water by Galvanic Cell; M. Kosaka, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Apr., 1992.

In situ Infrared Spectroscopic Stidies of Oxidation of P-Mercaptophenol; T. Sasaki and T. Ishikawa: *ibid.*, Apr., 1992.

In situ Infrared Reflection Absorption Spectroscopic Studies of Adsorbed Aromatic Thiols on Gold Polycrytalline Electrodes; T. Sasaki and T. Ishikawa: The First West Pacific Electrochemistry Symposium, May, 1992.

Inhibition Action of Benzotriazole and Its Derivatives on Corrosion of Copper in 3% NaCl Solution; Xiao-yan Liu, Guo-ding Zhou, T. Notoya and Mei-lun Shi: *ibid.*, May, 1992.

Development of Cathodes for Aluminum-chlorine Fuel Cell in High Temperature Chloride Melts; T. Ishikawa, T. Sasaki and S. Konda: The 8th International Symposium on Molten Salts, May, 1992.

Synthesis of K_2TiCl_6 and Its Stability in the Melt Mixture with NaCl; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The '92 Hokkaido Section Spring Meeting of JIM, June, 1992.

Equilibrium Constants for Dissolution of Several Chloride in Low-temperature $AlCl_3$-NaCl Melts; M. Noguchi, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, June, 1992.

Corrosion Behavior of Pb-Sn Alloys in Sulfuric Acid; M. Tomioka, M. Takahashi, T. Sasaki and T. Ishikawa: *ibid.*, June, 1992.

Copper Chelators: Its Possibility as Anti-fouling Reagents; T. Notoya: Seminar on Anti-fouling Measures Organized by Electrochemical Society of Japan, June, 1992.

Inhibition of Localized Corrosion in Copper Tubing by Pretreatment with 2-Undecylimidazole; T. Notoya: Conference of Advances in Corrosion and Protection, Manchester, June-July, 1992.

Localized Corrosion in Copper Tubes and Its Preventive Measures; T. Notoya, T. Ioue, F. Takagi, K. Nagata, T. Minamoto, H. Baba, T. Atsumi, T. Isobe, M. Watanabe, F. Hidaka and M. Kodaira: International Symposium on Control of Copper and Copper Alloys Oxidation, Rouen, July, 1992.

The Effect of Benzotriazole and Its Phosphonic Derivatives on Dissolution of Copper; T. Notoya, N. Sugii and T. Yamauchi: The 12th Meeting of Japan Rust Prevention Association, July, 1992.

Potential Variation in IRRAS Spectra of Thiols Adsorbed on Gold Polycrystalline Electrodes; T. Sasaki and T. Ishikawa: The '92 Fall Meeting of the Electrochem. Soc., Japan, Sep., 1992.

Behavior of Thiourea Adsorbed on Gold Electrodes as Monitored with in situ Infrared Reflection Absorption Spectroscopy; T.

Sasaki and T. Ishikawa: *ibid.*, Sep., 1992.

Effects of Dissolved Oxygen on Corrosion of Steel in Tap Water; M. Kosaka, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Sep., 1992.

Preparation of High-temperature Chloride Melts Containing K_2TiCl_6; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Sep., 1992.

Spot-tarnishing Prevention of Copper and Copper Alloys by Benzotriazole and Its Derivatives; T. Notoya, T. Ishikawa, F. Hidaka and T. Tsuji: *ibid.*, Sep., 1992.

Localized "Ant's Nest" Corrosion in Copper Tubing and Its Preventive Measures; T. Notoya, T. Inoue, K. Nagata, T. Minamoto, T. Atsumi, T. Isobe, M. Watanabe, F. Hidaka, M. Kodaira and F. Takagi: CORROSION ASIA, Singapore, Sep., 1992.

Galvanic Corrosion of Copper Pipes Connected with Steel Pipes T. Notoya: The Sprinkler Committee of Copper Development Association of Japan, Sep., 1992.

On the Infrared Reflection Absorption Spectra of Thiols Adsorbed on Gold Polycrystalline Electrodes; T. Sasaki and T. Ishikawa: The 86th Meeting of the Surface Finishing Society of Japan, Oct., 1992.

Anti-tarnishing of Copper and Copper Alloys by Surface Pretreatment; T. Notoya: The 32nd Meeting of Copper and Brass Research Association, Nov., 1992.

Spot-tarnishing of Copper and Copper Alloy Products; T. Notoya and T. Ishikawa: The '92 Hokkaido Section Fall Meeting of JIM, Nov., 1992.

Morphology of Co-deposited Al-Ti from Low-temperature Melts Containing Aluminum Chloride; N. Guo, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Nov., 1992.

Measurement Methods for Specific Gravity of $BaCl_2$-NaCl Melts; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Nov., 1992.

Infrared Reflection Absorption Spectra of Aromatic Thiols Adsorbed on Gold Polycrystalline Electrodes; T. Sasaki and T. Ishikawa: *ibid.*, Nov.. 1992.

Co-deposition and the Dissolved Forms of Several Metal Chlorides in Low-temperature Chloride Molten Salt Containing $AlCl_3$; M. Noguchi, S. Konda, T. Sasaki and T. Ishikawa: The 24th Symposium on Molten Salt Chemistry, Nov., 1992.

Procedures for Preparing High Temperature Chloride Melts Containing Titanium Tetrachloride; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The 4th JAPAN-CHINA Bilateral Conference on Molten Salt Chemistry and Technology, Nov., 1992.

Band Shifts of IR Spectra of Aromatic Thiols Adsorbed on Gold Electrodes with Potential Changes; T. Sasaki and T. Ishikawa: The 12th Seminar on Spectroscopic Studies of Adsorbed Molecules, Dec., 1992.

COMPOSITE MATERIALS PROCESSING AND EVALUATION LABORATORY

Prof. Dr. T. Narita, Assoc. Prof. Dr. Y. Ito,
Mr. Taumi, Mr. Matsuura and Mr. Yonezawa

Students

T. Mitsueda, S. Kawamori, T. Ida, E. Umekawa, S. Hayashi,
T. Sasaki, T. Yoshioka, S. Hata, M. Narumi, M. Nakano,
N. Fujimaru and M. Maeda

Associate professor Jiaju Guo from Beijing University of Science and Technology stayed as a visiting professor from April to November, 1992 and co-investigated on the aluminium nitride ceramic-metal joining. Mr. K. Miyama from NTK Ltd. joined at April, 1992 as a researcher on the Si_3N_4 ceramic-metal joining. Professors S. Mrowec and K. Danielvski from Poland visited and presented their lectures.

The research programs in our laboratory are :

(1) *Ceramic-metal joining*

Aluminum nitride or silicon nitride ceramics was joined to metals using both Ni-Cu-Ti and Ag-Cu-Ti solders and the thermal cycling test was carried out. Zirconia-Metal joinnings were investigated for development of SOFC.

(2) *High-temperature sulfidation of alloys*

Stainless steels were sulfidized in H_2-H_2S gas mixtures at 1073 and 1173 K, where Cr or Mn was selectively sulfidized to form internal sulfidation. This internal sulfidation was characterized by the preferential attack along alloy grain boundary. Mechanisms of these internal sulfidation phenomena were discussed from thermodynamic and kinetic considerations.

(3) *Ultrasonic Micro-Spectroscopy*

Scanning acoustic microscope (HITACHI 1000 S) was used to measure the thermal residual stresses by making use of the principle concept basing on the surface acoustic wave velocity and its change with stresses. This novel method was successfully applied to the ceramic-metal joint as well as the ion-exchanged glass. This was further extended for simultaneous measurements of stress and surface distortion of the ceramic-metal joints and other composite materials.

(4) *Coloration process of zirconia ceramics*

Zirconia ceramic was found to be degraded in accompanying with coloration phenomena when it was joined to metal using a Cu-Ag-Ti solder.

(5) *Computer simulation of 3-D grain size distribution*

Computer simulation process was developed in order to predict the three dimensional grain sizes and distribution from the cross-section, two dimensional observation of polycrystal materials.

(6) *Ceramic-metal composites*

Zirconia ceramics and Co-Ni-Cr-Al-Y powders were sintered in the plasma assisted hot-pressing and the plasma spray coating techniques in both air and vacuum in order to make the composite materials for thermal barrier coatings. Thermal expansion coefficients were measured as functions of temperature and composition as well as density and Young modulas were also measured.

Oral Presentation

Computer simulation of internal sulfidation phenomena; S. Kawamori and T. Narita: The 27th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1992.

Coloration phenomena of stabilized zirconia joined to metals; T. Mitsueda and T. Narita: *ibid.*, Jan., 1992

Thermal expansion measurements of the zirconia and CoNiCrAlY composite sintered by a PAS method; S. Taumi, M. Kamada and T. Narita: The 110th Annual Meeting of JIM, Apr., 1992

Electrical conductivity measurements of the coloration zirconia;

T. Mitsueda and T. Narita: *ibid.*, Jan., 1992

Evaluation of size distribution of sphere precipitates; K. Matsuura, M. Kubota and T. Narita: *ibid.*, Apr., 1992

Growth kinetics of the internal sulfidation for the Fe–Cr alloy; S. Kawamori and T. Narita: *ibid.*, Apr., 1992

Three dimensional size distribution of the precipitates evaluated from two dimensional observation; K. Matsuura and T. Narita: The Meeting of the Hokkaido Section of Jap. Inst. Iron and Steel, May, 1992

Monte-calro simulation of the grain growth from the ⟨110⟩ textures; Y. Ito, K. Matsuura and T. Narita: *ibid.*, June, 1992

Evaluation of the three dimensional size distribution of the solid-solid composite; K. Matsuura, Y. Ito and T. Narita: *ibid.*, June, 1992

Non-destructive evaluation of fracture strength of the Ionexchanged glass by acoustic microspectroscopy; H. Umekawa, T. Sasaki and T. Narita: The Spring Meeting of Hokkaido Section of Jap. Inst. Metals, June, 1992

Thermal cycling behavior of the ceramic-metal composities; H. Taumi and T. Narita: *ibid.*. June, 1992

Thermal cycling behavior of the Si_3N_4-metal joints; S. Hayashi and T. Narita: *ibid.*, June, 1992

Hot shortness of austenitic stainless steels; Y. Ito: Seminar of The Hokkaido Section of Jap. Inst. Iron and Steel, July, 1992

Grain size distribution of stainless steels separated by the grain boundary selective etching method; K. Matsuura, Y. Ito and T. Narita: The 111th Annual Meeting of JIM, Oct., 1992

Monte-calro simulation of the unusual grain growth; Y. Ito, K. Matsuura and T. Narita: *ibid.*, Oct., 1992

Evaluation of the ion-exchanged glass by acosutic microspectroscopy —(Part 2)—; H. Umekawa and T. Narita: *ibid.*. Oct., 1992

Effect of thermal treatment of the Zirconia-metal joints on their strength; T. Mitsueda and T. Narita: *ibid.*, Oct., 1992

Deformation behavior of the Si_3N_4/metal joint during thermal cycling treatments; S. Hayashi and T. Narita: *ibid.*, Oct., 1992

High-temperature stability of the ceramic-metal composites; H. Taumi and T. Narita: *ibid.*, Oct., 1992

High-temperature oxidation of silicon nitride ceramics —comparison between Al_2O_3 and Y_2O_3 additivies—; T. Sasaki and T. Narita: *ibid.*, Oct., 1992

High-temperature sulfidation behavior of Ti–Al alloys; T. Yoshioka and T. Narita: *ibid.*, Oct., 1992

Kinetics of grain boundary sulfidation for the Fe–36Cr alloy; S. Kawamori and T. Narita: *ibid.*, Oct., 1992

Kinetics of peritectic reaction in the Fe–C system; K. Matsuura, Y. Ito and T. Narita: The Fall Meeting of the Hokkaido Section of Jap. Inst. Iron and Metal, Nov., 1992

Effect of Pretreatment with Chromic Acid, Potassium Dichromate and Bonzotriazole on Corrosion of Copper and Copper Alloys

T. Notoya

Journal of the Japan Copper and Brass Research
Association 1992 Vol. 31 p. 32

Immersion tests and potentiostatic polarization measurements have been carried out to study the effect of the surface pretreatment of copper and two copper alloys with aqueous chromic acid (CrO_3) and/or benzotriazole (BTA), or potassium dichramate ($K_2Cr_2O_7$) solutions on corrosion of the materials in 0.1 M HCOONa solutions at 30°C. The metals used were oxygen free high purity copper (OF copper), phosphor bronze (P bronze) and beryllium copper (Be copper). The prefilming treatment with the aqueous inhibitor solutions conferred significant protection to the metals in neutral solution (pH 6.60), whereas the pretreatments gave less effective in acidified solution (pH 3.13). The best protection was provided to the metals by $K_2Cr_2O_7$ treatment (2% $K_2Cr_2O_7$ at 60°C for 1 hr). The overall performance of the surface pretreatments with aqueous BTA was found to be superior to that with CrO_3- or with the CrO_3 plus BTA-double treatment for P bronze and Be copper. For protecting dissolution of OF copper, the double treatment was more effective than the BTA- or CrO_3-single treatment. The potential E-log i relationships show that the prefilming treatments cause suppression of cathodic process more pronounced than that of anodic process for OF copper, while both the cathodic and anodic processes were suppressed for P bronze and Be copper. (Japanese)

Localized "ANT NEST" Corrosion of Copper Tubing and Preventive Measures

Takenori Notoya

Kinzoku No. 2 (1992) p. 23

An unusual form of copper tube corrosion has been detected early in service and in leakage tests after manufacturing. The morphology of this corrosion is similar to an "ant nest" when viewed in cross-section. This paper presents cases of the premature failure of copper tubes, simulation tests, corrosion mechanisms and preventive measures. (Japanese)

Mechanisms of Localized Corrosion in Copper Tubes

Takenori Notoya

Bulletin of the Faculty of Engineering Hokkaido
University, No. 162 (1992) p. 45

The mechanisms of a localized corrosion in copper tubes, so-called "ant's nest corrosion", are reviewed. Corrosives are carboxylic acids such as formic acid and acetic acid which are decomposition products of chlorinated hydrocarbons used for detergents and for lubricant oil used for bending processes. Possible corrosives are also presented. The influence of such factors as temperature, moisture, oxygen, the type of corrosives and its concentration, pH, the catalytic activity of copper surface, impurity of copper, bacteria and capillery forces are discussed. Corrosion processes are believed to be a mocro anode-macro cathode type corrosion of copper. Corrosion reactions include copper complex formation and its oxidation to produce cuprous oxide deposited in microtunnels in copper tubes and release acids in the pits, which accelerate the corrosion. (Japanese)

Formation of a $LaCrO_3$ Particle Dispersed Alloy Layer as a Means for Improving Oxidation Resistance

Hidetaka Konno and Ryusaburo Furuichi

High Temperature Corrosion of Advanced Materials
and Protective Coatings, p. 177-184, Elsevier
Sci. Pub., Amsterdam, 1992

At elevated temperature, perovskite structure $LaCrO_3$ is electron conductive and resistant to oxidation. A method to form a $LaCrO_3$ particle dispersed alloy layer by laser irradiation was developed. The method consists of (i) the formation of precursor films, $LaOHCrO_4nH_2O$, on metals by cathodic deposition from chromate solutions containing La(III) ions, (ii) heat treatment of the precursor films, and (iii) the simultaneous conversion of the precursor films to $LaCrO_3$ particles and the formation of the $LaCrO_3$ dispersed layer by CO_2 laser irradiation. The Type 430 and 304 stainless steels treated in this manner showed marked improvement in oxidation resistance, though a high yield of perfectly treated specimen has not been achieved, mainly due to technical problems. One Type 430 steel specimen showed only 5.8 g/m^2 of mass gain after 24.5 h oxidation at 1000°C in 0.20 atm H_2O-air : this mass gain was caused by the formation of an oxide nodule on a corner and the other parts of the specimen showed no accelerated oxidation. A Type 304 steel specimen showed no spalling after 10 cycles of oxidation in air for 60 min at 1100°C and cooling to room temperature, and the final mass gain was 3.2 g/m^2. Further development of the method is in progress.
(English)

Surface Reactions at 300–750 K in the Iron-Oxygen-Water System Studied by SIMS

G. Hultquist, M. Seo. Q. Lu, G. K. Chuah
and K. L. Tan

Applied Surface Science, **59,** 135–145 (1992)

Secondary ion mass spectroscopy, SIMS, has been applied to the surface study of the iron-oxygen-water system in the 300–750 K temperature range in order to gain insight into the initial stages of wet oxidation of iron. During sputtering with Ar^+ ions the emission of OH-containing ions was strongly dependent on temperature. In situ X-ray photoelectron spectrometry experiments were conducted in order to support this observation. In experiments where the metal was exposed simultaneously to $H_2{}^{18}O$ and $^{16}O_2$, the source of O in the reaction product could be determined by analysis of the ions emitted at different temperatures. This analysis showed that a coupled reaction, $2Fe+H_2O+\frac{1}{2}O_2\rightarrow 2FeOH$, is operating at room tempetature. At higher temperatures iron reacts preferentially with water as can be seen from the abundance of ^{18}O in the emitted ions. (English)

Pitting Corrosion Behavior of SiC/Al Alloy Matrix Composites

Kazuhiko Noda, Hitoshi Ono, Tooru Tsuru,
Hiroyasu Tezuka and Akihiko Kamio

J. Jpn. Inst. Metals, **56,** 641-647, (1992)

The corrosion behavior of SiC/Al Metal Matrix Composite (MMC) was investigated by polarization measurement and SEM observation. The behavior of SiC/Al MMC was the same as ordinary Al alloys as matrix materials. The anodic polarization curve of SiC/Al MMC in sodium borate-boric acid buffer solution (pH 8.39) containing sodium chloride was very similar to those of ordinary Al alloys. The pitting potential of SiC/Al MMC in each sodium chloride solution was almost the same as that of the ordinary alloys. This fact indicated that the existence of the SiC did not affect breakdown of the passive film.

According to the observation at the SiC/Al interface of model composites which contain macroscopic boundaries, small pits occurred at random over the whole surface after anodic polarization. Occasionally a small number of pits appeared at SiC/Al interface, suggesting the preferential sites for pit Growth.
(Japanese)

Kinetics and Mechanism of High-Temperature Sulfidation of an Fe-23.4Cr-18.6Al Alloy in H_2S-H_2 Atmospheres

K. Przybylski, T. Narita and W. W. Smeltzer

Oxidation of Metals, Vol. 38, Nos. 1/2, 1992, 1-32

Sulfidation of an Fe-23.4Cr-18.6Al (at. %) alloy was investigated in H_2S-H_2 atmospheres, $10^{-6} \leq P_{S_2} \leq 10^2$ Pa, at 973 K. It was found over this pressure range that sulfidation after an early transient period followed the parabolic rate law, being diffusion controlled. An investigation was carried out of the scales formed early transient sulfidation over the sulfur pressure range $p_{S_2} = 10^{-6}$ -10^{-2} Pa. Fully developed scales were multilayered consisting of an inner compact layer of equiaxed grains, an intermediate layer of equiaxed and columnar grains exhibiting a small degree of porosity, and an outer porous layer of distinct plates and needles. The grains of the inner and intermediate layer contained quaternary sulfide phases. The following phases were identified: spinels $(CrFe)Al_2S_4$ and $(FeAl)Cr_2S_4$, hexagonal $(FeCr)Al_2S_4$, $(CrAlFe)_2S_3$, and $(CrAlFe)_5S_6$. The plates and needles were composed of hexagonal $(FeCr)Al_2S_4$ and $(CrAlFe)_2S_3$ at $p_{S_2} = 10^{-6}$ and 10^{-5} Pa from which pyrrhotite, FeS, grew at $p_{S_2} \geq 10^{-4}$ Pa. The alloy exhibited a small degree of internal sulfidation; the precipitates were Al_2S_3 doped with Cr and Fe. Marker measurements indicated that growth of the inner sulfide layer was supported by inward migration of sulfur. The morphological development of the scales at 973 K was similar to that obtained at 1073 and 1173 K. (English)

Sulfidation Properties of Low Alloy Steels in H_2S-H_2 Atmospheres

Toshio Narita, Tatsuo Ishikawa
and Masaharu Nakamori

High Temperature Corrosion of Advanced Materials and
Protective Coatings, Vol. 1 (1992), 155-161

Sulfidation behaviors of low alloy steels, STBA 24 and STB 42, as well as the standard alloys of Fe-2.25Cr, Fe-2.25Cr-1Mo, Fe-1Si and -2Si alloys were investigated in H_2-H_2S gas mixtures at a themperature range from 673 to 973 K, as a series of investigations on the H_2S induced corrosion in the boiler furnaces. These STBA 24 and STB 42 alloys showed similar sulfidation kinetics and scale structures. Their sulfidation rates were 1/3 of those of Fe and standard Fe-2.25Cr and Fe-2.25Cr-1Mo alloys, and were close to those observed for Fe-1Si and Fe-2Si alloys. Sulfide scales were composed of duplex- or triplex-structures, that is, a duplex of inner and outer layers at high temperatures and a triplex layers of outer, intermediate, and inner layers at low temperatures. The outer and intermediate layers were compact, consisting of (Fe, Mn)S and (Fe, Cr, Mn)S phases, respectively. The inner layer was porous, and at high temperatures it was composed of a (Fe, Cr, Mn)S phase and metallic islands containing Si and Mo, with Si predominantly near the alloy/inner layer interface at low temperatures. The slow sulfidation rates observed for both the STBA 24 and STB 42 alloys are due to the effect of minor element like Si, but not major alloying elements like Cr and Mo. (English)

Development of Cathods for an Aluminum-Chlorine Fuel Cell in High Temperature Chloride Melts

Tatsuo Ishikawa, Takeshi Sasaki
and Shoichi Konda

Proc. 8th Internat. Symp. on Molten Salt,
92-16, 174-183 (1992)

An aluminum-chlorine fuel cell for manufacturing aluminum chloride was proposed as one process of an electrochemical cycle for production of high-purity aluminum from aluminum scraps. To develop cathodes for the fuel cell, several graphite electrodes with many holes of the same size were tested by changing the hole sizes and numbers, and the performance for the reduction reaction of chlorine was estimated in terms of the discharge characteristics of the cell in a mixture of $MgCl_2$ 25 mol%-NaCl 75 mol% at 750°C. The voltage drops due to the resistance of the reduction reaction decrease with the decrease in the size of the holes, but in small holes such as those 2 mm in diameter hardly all holes worked equally, showing the difficulty of enlarging the reaction zone. To overcome this disadvantage of drilled electrodes, grooved electrodes were developed and an output current of 4 A at an output voltage of 1.5 V was attained using electrodes with a diameter of 68 mm.

Study on Anodic Deposition of Ferrous Ions on Gold by a Quartz Crystal Microbalance

M. Seo. K. Yoshida, H. Takahashi and I. Sawamura

J. Electrochem. Soc., **139,** 3108-3111 (1992)

In situ quartz crystal microbalance (QCM) technique has been applied to investigate anodic deposition of ferrous ions on gold in solutions containing different electrolytes (perchlorate, phosphate, and borate) with relation to the formation of passive films on iron. The apparent molecular weight of deposited films was evaluated from comparison between *in situ* QCM and coulometry and was found to depend strongly on the electrolyte composition. The electrolyte dependence on apparent molecular weight was attributed to anodic oxidation of ferrous complex ions which were formed by the reaction of ferrous ions and electrolyte anions. (English)

Electrochemical Formation of Protective Oxide Coatings on Steels to Improve Resistance to High Temperature Oxidation

Hidetaka Konno

Proc. ASEAN-Japan Cooperation on Materials Science and
Technology, Seminar/Workshop on Corrosion of Metals,
Manila, Philippines, pp. 1 (1992)

It is well known that the surface incorporation (or doping) of active elements such as rare earths, Ti, Zr, Nb to Cr and/or Al containing alloys lead to the marked enhancement in their resistance against high temperature corrosion in oxidizing atmospheres. In the present paper, three types of cathodic deposition methods to form mixed or composite oxide films containing active elements on stainless steels are introduced: each method forms different types of oxide films by different mechanisms. The oxidation inhibition performances of the films examined by isothermal oxidation in a 0.2 atm H_2O-air atmosphere at 1000°C and by cyclic oxidation in air at 900°C are also demonstrated. (English)

Formation of Aluminium Yttrium Mixed Oxide Film by Electrodeposition

Hidetaka Konno, Rina Segawa, Isao Saeki
and Ryusaburo Furuichi

J. Surf. Finish. Soc. Jpn, **43,** 720 (1992)

A method to form aluminium-yttrium mixed oxide films by cathodic deposition was developed and oxidation resistance of the oxide coated stainless steels was evaluated. (Japanese)

Composite Oxide Films Formed by Electrochemical Process

Hidetaka Konno

DENKI KAGAKU, **60**, 861 (1992)

Cathodic and anodic polarization methods to form composite oxide films on metals were introduced and reviewed. (Japanese)

In-situ XPS Study of Zirconium Oxide Promoted by Platinum and Sulfate Ion

Kohki Ebitani, Hidetaka Konno, Tsunehiro Tanaka
and Hideshi Hattori

Journal of Catalysis, **135,** 60-67 (1992)

In-situ X-ray photoelectron spectroscopy (XPS) and infrared (IR) study of adsorbed CO were performed to characterize the states of the platinum particles supported on the sulfate ion-treated zirconium oxide (SO_4^{2-}-ZrO_2) after reduction with hydrogen. Presence of the sulfate ion strongly suppressed the reducibility of the platinum particles as well as the chemisorptive capacity for CO. The platinum particles consisted mainly of platinum cations (mixture of platinum oxide and platinum sulfate) after reduction with hydrogen at 673 K; the concentration of metallic platinum phase was low. The low reducibility of the dispersed platinum particles present as platinum cations on the SO_4^{2-}-ZrO_2 support is interpreted by the redox metal-support interaction (RMSI), which is caused by the acidic properties of the SO_4^{2-}-ZrO_2 support and results in a slow nucleation of the platinum particles. The states of sulfur were also measured by XPS, and the partial conversion of the S^{6+} (sulfate ion) to S^{2-} species on hydrogen treatment is concluded to occur by the metal-catalyzed mechanism involving spiltover hydrogen atoms resulting from the dissociation of a hydrogen molecule on the metallic platinum. (English)

Electrochemical Formation of A-Site Substituted Perovskite Structure $La_{1-x}M_xCrO_3$ Oxide Coatings

Hidetaka Konno, Masahiro Tokita, Atsushi Furusaki
and Ryusaburo Furuichi

Electrochimica Acta, **37,** 2421 (1992)

A method to form A-site substituted perovskite structure lanthanum chromium oxide coatings on metals has been developed. Precursor films having compositions of $(LaOH)_{1-x}M_xCrO_4 \cdot nH_2O$ were formed on metals by cathodic polarization in chromate solutions ($pH=1.8$-2.8) containing $La(NO_3)_3$ and $M(NO_3)_2$[M=Ca or Sr]. The formation of the precursor films is explained by association and precipitation reactions of $LaOH^{2+}$, CrO_4^{2-} and M^{2+} ions which were formed at the cathode surface due to the rise in pH caused by hydrogen evolution and the reduction of NO_3^- ions. The formation conditions with Ca(II) $x<0.1$ and with Sr(II) $x<0.2$ were determined on chemically polished Ni. The conditions for precursor on type 304 stainless steel have also been surveyed. The precursors were converted into perovskite structure $La_{1-x}M_xCrO_3$ by pyrolysis in a N_2 atmosphere. The temperature and timeof the pyrolysis depended on the substituted ion, M, and the x value. (English)

Anodic Oxide Film Formation on ADC12 Aluminum Die-Casting Alloys in A Sulfuric Acid Solution

Hideaki Takahashi

Special Issue on Surface Treatment of ADC12 Aluminum
Die-Casting Alloy Surf. Treatment Soc. of Aluminum
Die Castings, p 121-136, (1992)

Anodic Oxidation of ADC12 aluminum die-casting alloy in a sulfuric acid solution has been reviewed.

Distinctive features on the film formation on ADC12, which are a) high anode potential, b) low current efficiency for film formation, c) formation of oxide films with non-uniform thickness and with dark-brown color, were explained in terms of the microstructure of the metal substrate, by comparing the data obtained from rapidly solidified alloys and casting alloys. (Japanese)

Oxide Films Formed on Aluminum by Duplex Thermal/Anodic Processsces

—Effect of Pretreatment—

Hideaki Takahashi, Chiko Ikegami
and Masahiro Seo

Proc. of Symp. on Oxide Films on Metals and Alloys,
Electrochem. Soc. **92-22,** 414-427 (1992)

Formation of anodic oxide films on aluminum with electropolishing, H_3PO_4/CrO_3- and NaOH-immersion treatment, followed by thermal oxidation at 823 K has been investigated by electrochemical measurements and electron microscopy.

It was found that thermal oxidation of H_3PO_4/CrO_3-treated specimens was slower than other specimens, and that the terminal thickness of thermal oxide films was ca. 30 nm, independent of the kind of pretreatment.

The anodic oxide films formed on all the 3 hr heated specimens showed a crystalline one layer structure, the thickness of which was proportional to the anode potential with 0.77 nm V^{-1} as the proportionality constant. The anodic oxide films on electropolished and H_3PO_4/CrO_3-treated specimens included appreciable amounts of voids and cracks. The apparent dielectric constant of the anodic oxide films was observed to be 10-34, depending on the anode potential. This is discussed in terms of the penetration of electrolyte into voids in the oxide after anodizing. (English)

Study on Anodic Deposition of Ferrous Ions on Gold in Aqueous Solutions Containing Chloride Ions by a Quartz Crystal Microbalance

Masahiro Seo and Kengo Yoshida

Proc. 12th Scandinavian Corrosion Congress
& Eurocorr '92, Vol II, p 367–p 372 (1992)

An in-situ quartz crystal microbalance (QCM) technique has been applied to investigate the formation process of deposited films on gold due to anodic oxidation of ferrous ions in solutions containing chloride ions, with relation to the formation of passive films on iron. The apparent molecular weight of the deposited films was evaluated from a comparison between in-situ QCM and coulometry, and it did not strongly depend on the concentration of chloride ions within the reproducibility of the experimental data. The composition of the deposited films corresponding to the apparent molecular weight was a partially hydrated ferric oxy-hydroxide, $FeOOH \cdot nH_2O$ ($n=0-1$), when no chloride ions were incorporated in the films. (English)

Formation of Perovskite Type $LaCrO_3$ by Pyrolysis of La(III)-Cr(VI) Precursor

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Ryusaburo Furuichi

J. Chem. Soc. Jpn., 612 (1992)

Perovskite type lanthanum chormium oxide, $LaCrO_3$, was prepared by pyrolysis of $La\cdot(CH_3COO)(CrO_4)\cdot nH_2O$ ($n \fallingdotseq 2$) precursor which was obtained as residue of the evaporation of an equimolar mixture of lanthanum acetate and chromium trioxide. The pyrolysis process was investigated by TG-DTA, XRD, IR, EPR, chemical analysis, and elemental analysis. It was found that pyrolysis reaction of the precusor is affected by partial pressure of oxygen, P_{O_2}, in the atmosphere. An increase in P_{O_2}, caused a change in mass loss-temperature curves from a one-step to a two-step type (Figs, 3, 8). For $P_{O_2} \geqq 0.10$ atm, the reaction clearly proceeded in two steps via the formation of monoclinic $LaCrO_4$ as an intermediate (Figs. 4, 5). The first step was corresponded to the combustion of acetate moiety in the precusor and crystallization to form $LaCrO_4$, and the second step was an elimination of the oxygen of $LaCrO_4$ and the phase trannsition to orthorhombic $LaCrO_3$. For $P_{O_2} \leqq 0.028$ atm, $LaCrO_3$ was formed by the one-step reaction, and the transition temperature to $LaCrO_3$ was lower than at higher P_{O_2} (Fig. 8). The intermediate compound, $LaCrO_4$, was obtained as a single phase at 575～625°C in air, and it was stable at 600°C for at least 12 h (Fig. 10). Specific surface area of $LaCrO_3$ formed by 3 h pyrolysis at 650°C in N_2 was $19 \pm 2\ m^2\cdot g^{-1}$.

A-site substituted perovskite type oxide could also be prepared by a similar method: $La_{0.8}Ca_{0.2}CrO_3$ was prepared by pyrolysis at 800°C for 5 h in N_2 from the precursor, which was obtained from a mixture of lanthanum acetate, calcium carbonate, and chromium trioxide (Fig. 14). (Japanese)

Ion-Exchange Adsorption Affnity of Lithium Ions for Surface Hydroxyl Groups on Manganese Dioxide

Noriaki Katayama, Hiroki Tamura
and Ryusaburo Furuichi

Bunseki Kagaku, **40**, 635 (1992)

The affinity of lithium ions for manganese dioxide was measured by titration, and it was compared with other alkali metal ions. The amounts of adsorbed alkali ions increased with pH. At lower pHs the amount of adsorbed lithium ions was similar to or rather smaller than the other ions, but with increasing pH it became the largest and the order was $Li^+ > Na^+ > K^+ > Cs^+$. The adsorption of alkali metal ions, M^+, on manganese dioxide is due to the ion exchange with protons of surface hydroxyl groups of manganese dioxide, $\equiv MnOH$,

$$\equiv MnOH + M^+ \rightleftharpoons \equiv MnO^- \cdot M^+ + H^+$$

The equilibrium condition of this reaction is given by the Frumkin equation.

$$K^\circ = K\exp(A\theta)$$

where K° is the intrinsic equilibrium constant, K the concentration ratio $([\equiv MnO^- \cdot M^+][H^+]/[\equiv MnOH][M^+])$, A the electrostatic interaction constant between the absorbed ions with the same charge, and θ the coverage. The exponential term is the activity coefficient of adsorbed ions and expresses a suppression of ion exchange due to electrostatic repulsion between ions with the same charge. The values of K° and A were determined by fitting the equation to the experimental data, and they were in the order $Li^+ < Na^+ < K^+ < Cs^+$. The reactivity of lithium ions for manganese dioxide (K°) is smaller than the other ions, but with increasing pH the adsorption of lithium ions increases more steeply because the suppression due to electrostatic repulsion (A) is smaller than the other ions. The differences in the K° and A values of alkali metal ions are discussed in terms of the hydration of the ions. (Japanese)

Mechanism of Incorporation of Impurity Metal Ions in EMD

H. Tamura, K. Ishizeki and R. Furuichi

Progress in Batteries & Battery Materials, **11,** 47 (1992)

The amount of impurity metal ions incorporated in manganese dioxide (EMD) during electrolysis increased in proportion to the concentration in solution, and the amount of incorporation at a fixed concentration varied widely from ion to ion in the order $Fe^{3+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. With increasing anodic current density, the amount of incorporated Fe^{3+} decreased, but the incorporated divalent ions increased. The anode potential and the specific surface area of the formed EMD increased with increasing anodic current density. The affinity order of ions for the MnO_2 surface coincided with the incorporation order as above. The mechanism of incorporation was discussed by considering that the incorporation occurs through adsorption of ions on growing EMD particles. The effect of anodic current density on incorporation was explained in terms of the combined effects of increasing anode potential and increasing specific surface area on adsorption. (English)

CRGHU

Confirmation of the Fleischmann-Pons Effect (Relationship between reaction products and D/Pd loading ratio)

Tadahiko Mizuno, T. Akimoto, K. Azumi
and M. Enyo

Proceedings of the Fourth International ISEM Syposium
on Nonlinear Phenomena in Electromagnetic Fields
Nagoya, Japan, 26-29 January, 1992
Supplement to Volume 3 of the International Journal
of Applied Electromagnetics in Materials

New observations on the neutron, tritium and heat evolution with particular concern on the deuterium loading ratio Pd electrode immersed in D_2O solution in a perfectly sealed cold fusion cell are reported. The ratio of neutron emission at 2.45 MeV, tritium production and heat generation observed were $n : T : H = 1 : 10^4 : 10^{12}$. Deuterium loading ratio of the Pd electrode strongly affects on the reaction products.

Diffusion Rate of Deuterium in Pd during Cathodic Charging

T. Mizuno, T. Akimoto, K. Azumi and M. Enyo

The Electrochemical Society of Japan
60 405～411, (1992)

The kinetics of absorption and release of deuterium for Pd during cathodic electrolysis were analysed using a closed cell. The cell was made of stainless steel and having a Pt black recombination catalyst, a pressure to voltage transducer, three thermo couples and several electrode; In–situ observation of D/Pd ratio possible and it can be analysed the condition between Cold Fusion reaction and deuterium behaviour in the metal. At least two states of deuterium in Pd are deduced from the behaviour of the diffusion. The difference in diffusion constant is by two orders of magnitude, being of the order of 10^{-6} and 10^{-8} cm^2/s, respectively, at room temperature. It is supposed that the α, β and a new phases contribute to the diffusion processes in these two fast and slow steps respectively.

In Situ Infrared Reflection Absorption Spectroscopy of Aromatic Thiols Adsorbed on Gold Electrode

Takeshi Sasaki and Tatsuo Ishikawa

J. Surface Finishing Soc. Japan, **44,** 457–461 (1992)

In order to acquire spectra of organic materials adsorbed on electrode surfaces by *in situ* infrared reflection absorption spectroscopy, several new techniques have been developed. The spectra of 2, 5-dihydroxythiophenol (DHT) and p-mercaptophenol (MP) adsorbed on polycrystalline gold electrodes were measured as a function of potential using these new *in situ* IRRAS techniques.

The techniques developed in this work made it possible, in the fingerprint region, to monitor the changes in the vibrational properties of monolayer-adsorbed DHT and MP as a function of the applied potential. The overall spectral characteristics of both DHT and MP and their quinone derivatives in the absorbed state closely resemble those of their solution-phase counterparts. The relatively high intensity of the signals observed for the adsorbed species provides strong evidence that both DHT and MP are adsorbed on gold with the molecular plane nearly perpendicular to the electrode surface and that their oxidation states change with potential change. (Japanese)

Characterization of Lanthanum (III) Chromium (V) Tetraoxide by X-ray Photoelectron Spectroscopy

Hidetaka Konno, Hiroto Tachikawa, Atsushi Furusaki
and Ryusaburo Furuichi

Anal. Sci., **8**, 641 (1992)

Lanthanim(III) chromium(V) tetraoxide, $LaCrO_4$, was synthesized by a thermal decomposition method and characterized by X-ray photoelectron spectroscopy and *ab initio* molecular orbital calculations. The chromium(V) state in $LaCrO_4$ is stable both in air and vacuum. The electron binding energies, E_B, and Auger parameters, α, of Cr(V) and La(III) indicated that the covalency of the Cr–O bonds in CrO_4 tetrahedra is higher than that in CrO_6 octahedra of $LaCrO_3$, and that La(III) in $LaCrO_4$ is more ionic than in $LaCrO_3$. The results of *ab initio* molecular orbital calculations agreed with the measured characteristics, that is the electrons are flowing from oxygen to Cr(V) and the covalency plays a significant part in the Cr–O bonds. This behavior of the Cr–O bond was considered to contribute stabilizing CrO_4^{3-} tetrahedra. (English)

Stability Constants and Structures of Uranyl and Thorium Chloro-Complexes

Hiroshi Ohashi and Takashi Morozumi

RARE EARTHS-Materials of the 21st century, p. 462–463.
The Rare Earth Society of Japan (1992)

Stability constants of uranyl and thorium chloro-complexes decrease rapidly with increasing ionic strength. The ionic complexes are typical outer-sphere complexes as the Fuoss formula is applicable to this relationship and the heat of formation is remarkably small. The thermodynamic equilibrium constants of 33 and 212 mol^{-1} l were also determined for these chloro-complexes.

A dumbbell configuration of the uranyl ion was assumed to explain the ionic strength dependence of the stability constant of uranyl chloro-complex. In this model, the chloride ion interacted electrostatically with each of the uranium and oxide ions. The inter ionic distance was evaluated to be 0.30 nm between the uranium and chloride ions. The distance suggests that one of water molecules coordinating with the uranium ion is replaced by a chloride ion and that a complex of the type $UO_2(H_2O)_3Cl^+$ is formed. Further, the inter-ionic distance of 0.40 nm was obtained for the thorium chloro-complex, and the complex of $Th(H_2O)_6Cl^{3+}$ was proposed.

Piezoelectric Response to Surface Stress Change of a Palladium Electrode in Sulfate Aqueous Solutions

Masahiro Seo and Masaki Aomi

J. Electrochem. Soc., **139**, 1087-1090 (1992)

The interfacial properties of palladium electrode in sulfate solutions of different pH values have been investigated using the piezoelectric response of surface stress change induced by a potential modulation. It was found from the piezoelectric signals that the potential of electrocapillary maximum, E_{max} or potential of zero charge (pzc) is present in the potential region of hydrogen absorption into Pd. The pH dependence of pzc was measured in the range from pH 0.7 to 12.8. Below pH 6.0, pzc was close to the equilibrium potential of hydride formation. Above pH 6.0, pzc was higher than that of hydride formation. The piezoelectric signals obtained in the potential region of oxide formation suggested that sign-reversal of surface charge takes place in the potential range of PdO monolayer formation which is similar to Pt electrode.
(English)

Reaction-Layer of Silicon-Nitride Ceramics to Metal Joints Using Ni-Base Solders

Toshiyuki Takashima, Tsuyoshi Yamamoto
and Toshio Narita

Journal od the Ceramic Society of Japan, Int. Edition,
Vol. 100 (1992), 913-917

Silicon nitride ceramics was joined to a stainless steel using a Ni-Cr-P amorphous solder (MBF 65) and two MBF 65 solders with Cr or Mn thin films vapor-deposited. Bonding layer were composed of a chromic silicate layer close to the ceramics surface and a duplex phases of a chromic nitride and a nickel solution containing small amounts of chromium and silicon. Growth of the bonding layer was parabolic at the initial stage and then slowed with decreasing in chromium contents in the solder. A parabolic rate constant of the joints with the MBF 65 and MBF 65-Mn solder was $1.0 \times 10^{-15}\ m^2 \cdot s^{-1}$ at a temperature of 1333 K. Fracture strengths increased with decreasing in thickness of the bonding layer, that is, they were 50 to 140 MPa for the joint with a MBF 65 solder, 120 to 170 MPa for the joint with a MBF 65-Cr solder, and 130 to 200 MPa for the joint with a MBF 65-Mn solder. (English)

Simultaneous Measurements of Stress and Distortion of the Ceramic-Metal Joints by Scanning Acoustic Microscopy

Toshio Narita, Tatsuo Ishikawa
and Isao Ishikawa

Nondestr. Test. Eval., Vol. 8-9, pp. 709-716

Simultaneous measurements of stress and distortion of ceramic-metal joints were investigated using the scanning acoustic microscopy. The principle of the methodology is the measurement of the X-Z image, which is obtained by the synchronized movement of an acoustic lens in both the X- and Z-directions. This paper details the measurment and analytical procedures and provides results for silicon nitride ceramic-nickel joints, which were subjected to thermal cycles between room temperature and 1073 K. (English)