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For additional copies and more information, please write to the editors ;

Professor T. Ishikawa, Electrometallurgy Laboratory,
Professor M. Seo, Electrochemistry Laboratory,
Professor H. Ohashi, Nuclear Reactor Materials Laboratory,
Professor R. Furuichi, Analytical Chemistry Laboratory,
Professor T. Narita, Composite Materials Processing and Evaluation Laboratory.

Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8,
Kita-ku, Sapporo 060, Japan

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

Students

S. Ishiguro, T. Ikegami, K. Fushimi, M. Aomi, T. Itoh,
K. Shiga, I. Ninomiya, K. Fujiwara and K. Yoshida

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, hydrogen absorption, and metal finishing.

Piezoelectric Response to Surface Stress Change of Pd Electrode in Perchlorate Solutions Containing Chloride Ions

The interfacial properties of palladium electrode in perchlorate solutions containing chloride ions have been investigated from the piezoelectric response of surface stress change induced by a potential modulation. The potential of zero charge located in the potential region of hydrogen adsorption into Pd depended strongly on the chloride ion concentration. The sign reversal of surface charge which took place in the potential region of oxide formation was also influenced by the addition of chloride ions.

Membrane Potentials of Nickel Hydroxide and Its Mixed Hydroxides Prepared on Platinum Net Electrode

Nickel hydroxide and its mixed hydroxides were cathodically deposited on platinum net electrode from 0.1 M $Ni(NO_3)_2$ solution or + x M $Fe(NO_3)_3$. The membrane potentials of the hydroxides were measured in NaCl solutions with different concentrations (10^{-4} M − 1 M) to investigate the ion selective properties. The nickel hydroxide and its mixed hydroxides as received were anion-selective. The anodic oxidation of these hydroxides was perfomed in 1 M

KOH solution to investigate the changes of selective ion permeability.

QCM Study on Anodic Deposition of Ferrous Ions on Gold

A quartz crystal microbalance (QCM) technique was applied to investigate the anodic deposition process of ferrous ions on gold in solutions containing chloride ions. The apparent molecular weight of the deposited films was evaluated from a comparison between in-situ QCM and coulometry. The apparent molecular weight of the deposited films thus evaluated did not strongly depend on the concentration of chloride ions within the reproducibility of the experimental data, suggesting no significant incorporation of chloride ions into the films.

Electroluminescence from Metals during Anodic Oxidation

Electroluminescence (EL) was detected from Nb, and Ta during anodic oxidation in Na_2SO_4 aqueous solution to investigate the relation between the EL intensity and oxide film growth. The EL intensity detected under a galvanostatic condition increased rapidly with increasing anodic potential above 20 V, depending on the anodic current density. The broad EL spectra with a peak at about 420 nm were obtained in the wavelength range from 350 nm to 700 nm. Further experiments are being conducted to obtain the information on the defective structures of anodic oxide films from the EL measurements.

Formation of Porous Anodic Oxide Films on ADC-12 Die-Casting Alloy

Formation mechanism of porous anodic oxide films on ADC-12 die-casting alloy (Al-10.7Si-2.05Cu-0.91 Fe-0.16 Mn-0.10 Mg-0.49 Zn-0.04 Ni-0.01 Sn) has been investigated in sulfuric acid solutions by ICP-atomic emission spectroscopy, electron microscopy, and measurements of evolved-gas volume. The alloying elements of Cu, Fe, and Mn in the specimens were found not to affect the dissolution rate of film during anodizing, but to enhance the O_2-gas evolution rate considerably.

Anodizing of Aluminum Covered with Thermal Oxide Films

Electropolished aluminum specimens were immersed either in b) H_3PO_4/CrO_3 solution, or c) NaOH solution as pretreatment. The pretreated specimens were heated at 550°C for 3 hrs and then anodized in a neutral borate solution to examine the effect of pretreatments on the structure of anodic oxide films. The thermal-anodic oxide films formed after NaOH immersion was found to include much smaller amounts of voids than those after H_3PO_4/CrO_3 immersion. The apparent dielectric constant for thermal/anodic oxide films were estimated to be 10–30, and this was understood as results of the penetration of electrolyte into the voids.

Rectification Phenomena with Porous and Barrier Type Oxide Films/Aluminum/Solution Systems

Aluminum electrode covered with porous and barrier type oxide films were polarized by potential sweep method in a neutral borate solution and in a vacuum. The rectification on current was observed in the solution, but not in vacuum. Cathodic polarization in the solution caused the pits to form, and the number and diameter of pits increased as the cathodic current increased. The pit formation behavior was different between porous and barrier type oxide films.

Diffusion Process of Hydrogen in Palladium

Diffusion behavior of hydrogen in palladium foil was studied by using named FR (Frequency Response) method. The diffusion constant D_H of hydrogen in palladium was estimated to be ca. 3×10^{-7} cm^2 s^{-1} at 293 K, and the value decreased with hydrogen charging time. After hydrogen released by heating, D_H returned to original value. This result seems to indicate that the repulsion between hydrogen atoms affects the values of D_H.

Acoustic Emission from the Palladium Electrode

Acoustic emission (AE) from palladium electrode was measured during electrochemical hydrogen charging and discharging processes. A large amount of AE signal was observed for a few minute at hydrogen charging which seems to be concerned with Pd lattice deformation. Periodic AE signal was also observed at hydrogen release process which seems to reflect the periodic process between pressure increase at a defect and pressure decrease accompanied with hydrogen release from it.

In-situ STM Measurement of the Electrodes

Scanning Tunneling Spectroscopy (STM) equipment was developed for STM/STS measurement on electrode surface in electrolyte. A lock'in amplifier was also attached to STM system for AC conductivity measurement. About 1 nm resolution was achieved for measurement of platinum and gold sample. For titanium nitride sample a semiconductor property was obtained by tunneling spectroscopic measurement.

Other Activities

Prof. M. Seo attended the 180th Meeting of the Electrochemical Society which was held in Phoenix, Arizona, U.S.A. on October 13–18, 1991 and presented a paper entitled "Study on Anodic Deposition of Ferric Oxyhydroxide Films on Gold by a Quartz Crystal Microbalance". Afterward, Prof. M. Seo visited Corrosion Research Center, University of Minnesota, U.S.A.

Dr. Takahashi attended the 7th Asian-Pacific Corrosion Control Conference in Beijing, China on August 19–23, and presented a paper on the anodizing of aluminum die-casting alloy. After the conference, he visited General Research Institute for Nonferrous Metals in Beijing to discuss with Dr. Zhu et al. and to give a lecture on anodic oxide films on aluminum and its alloys.

The following scientists from over the sea visited this Laboratory in this year of 1991 : Dr. Isabel A. Raspini from University of Buenos Aires, Argentina on March 5, Professor Robert A. Rapp from The Ohio State University, U.S.A. on August 26, Prosessor Arthur T. Hubbard, University of Cincinnati, U.S.A. on Septenber 24, and Professor Rudiger Memming, Institute fur Solarenergieforschung, Gmbh, Germany on October 8.

Oral Presentation

Anodic Deposition and Cathodic Reduction of Ferric Oxyhydroxide Films on Gold by a Quartz Crystal Microbalance; I. Sawamura and M. Seo: The 17th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan., 1991

Breakdown of Anodic Oxide Films on p-Si due to Chloride Ions and Electroluminescence Measurement; K. Fushimi, H. Takahashi and M. Seo: *ibid.*, Jan., 1991

Tunneling Spectroscopy of the Passive Films; K. Araki, K. Azumi and M. Seo: The 17th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan., 1991

Electrochemical Study of Hydrogen and Deuterium in Palladium; T. Fujita, K. Azumi, T. Mizuno and M. Seo: *ibid.*, Jan., 1991

Piezoelectric Response to Metal Electrodes Covered with Oxide Films; M. Seo: The 26th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1991

Unique Behavior of ADC 12 Aluminum Die Casting Alloy (ADC 12) at Anodizing in Sulfuric Acid Solution; H. Takahashi, K. Watanabe and R. Furuichi and M. Seo: *ibid.*, 1991

Formation of Porous Anodic Oxide Films on ADC 12 and Al-Si-Cu Casting Alloys; K. Watanabe, H. Takahashi, R. Furuichi and M. Seo: The 1991 Winter Meeting of the Hokkaido Secs. of Jpn. Soc. Anal. Chem. and Chem. Soc. Jpn., Feb., 1991

Anodizing of ADC 12-Aluminum Die Casting Alloy; H. Takahashi, K. Watanabe, R. Furuichi and M. Seo: The 83rd Annual Meeting of the Metal Finishing Soc. Jpn., March, 1991

Electroluminescence Behaviors Associated with Breakdown of Anodic Oxide Films on Si due to Chloride Ions; K. Fushimi, H. Takahashi and M. Seo: The 58th Meeting of Electrochem. Soc. Jpn., April, 1991

Structural Analysis of Anodic Oxide Films Formed on Aluminum after Heat Treatment; H. Takahashi, C. Ikegami and M. Seo: The 52nd Annual Meeting of the Jpn. Soc. Anal. Chem., May, 1991

In-situ QCM Measurement of Anodic Deposition Process of Ferric Oxyhydroxide on Gold; M. Seo, I. Sawamura and H. Takahashi: '91 Spring of the Jpn. Soc. Corros. Eng., May, 1991

Formation Mechanism of Porous Anodic Oxide Films on ADC 12 Aluminum Die Casting Alloy; H. Takahashi, K. Watanabe, R. Furuichi and M. Seo: *ibid.*, May, 1991

Electronic Property of the Passive Films Measured by Tunneling Spectroscopy; K. Azumi, K. Araki and M. Seo: *ibid.*, May, 1991

Anodizing of Aluminum; H. Takahashi: Seminar on Introduction of Metal Finishing, Supported by Metal Finishing Soc. Jpn. June, 1991

Film Formation Mechanism of Anodic Oxide Films on Thermotreated Aluminum; H. Takahashi, C. Ikegami and M. Seo: The 1991 Summer Meeting of the Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. Anal Chem., July, 1991

Cathodic Polarization of Aluminum Covered with Anodic Oxide Films; H. Takahashi, K. Kasahara and M. Seo: *ibid.*, July, 1991

XPS Study on the Structure of Aluminum (Hydr-)oxides; T. Tsuchida and H. Takahashi: *ibid.*, July, 1991

Tunneling Spectroscopy in Electrolyte; K. Azumi: The 1991 Summer Seminar of Hokkaido Branch of the Metal Finishing Soc. Jpn., August, 1991

Measurement of Minute Corrosion of Copper Thin Films by a Quartz Crystal Microbalance; M. Seo: The First Meeting of Corrosion Protection Engineering in Hiroshima, Aug., 1991

Formation Mechanism of Porous Anodic Oxide Films on An Aluminum Die-Casting Alloy; H. Takahashi, K. Watanabe, R. Furuichi and M. Seo: The 7th Asian Pacific Corros. Control Conf., Aug., 1991

Introduction of Anodizing of Aluminum; H. Takahashi: Seminar at Beijing General Research Inst. for Non-Ferrous Metals, Aug. 1991

Piezoelectric Response to Surface Stress Change of Palladium Electrode; M. Seo: The 4th Intern. Symp. on Frontiers of Electrocatalysis, Sapporo, Japan, Sept., 1991

Measurement of Change in Surface Stress of Electrode by Potential Modulated Piezoelectric Response; M. Aomi and M. Seo: '91 Fall Meeting of Chem. Soc. Jpn., Sept., 1991

Impedance Change in Thermo-treated Aluminum during Anodizing; H. Takahashi, C. Ikegami and M. Seo: *ibid.*, Sept., 1991

Tunneling Spectroscopy of the Oxide Films formed on Electrode Surface in Electrolyte; K. Azumi, K. Araki and M. Seo: *ibid.*, Sept., 1991

High Electric Field Supporting Ability of Anodic Oxide Films on Aluminum; H. Takahashi: Meeting on Development of Wet Process, Sept., 1991

Study on Anodic Deposition of Ferric Oxyhydroxide Films on Gold by a Quartz Crystal Microbalance; M. Seo, I. Sawamura and H. Takahashi: The 180th Meeting of The Electrochemical Soc., Phoenix, Arizona, U. S. A., Oct., 1991

Structure and Properties of Composite Oxide Films on Aluminum; H. Takahashi: Memorial Symp. for Prof. G. E. Thompson on Electrochem. Behaviour of Alum. on Electrolytic Capacitor Production Tech., Oct., 1991

Study on UPD of Copper on Gold by Piezoelectric Response; M. Seo and X. C. Jiang: The 84th Annual Meeting of Metal Finishing Soc. Jpn., Nov., 1991

Anodic Oxydation of Thermo-treated Aluminum —Effect of Pretreatment—; C. Ikegami, H. Takahashi and M. Seo: *ibid.*, Nov., 1991

Thermal Oxidation of Aluminum and Anodic Oxidation of thermo-oxidized Aluminum; H. Takahashi, C. Ikegami and M. Seo: The 8th ARS Hakodate Meeting, Supported by Metal Finishing Soc. Jpn., Nov. 1991

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

Febrianto, H. Kobayashi, Y. Sugita, M. Yoneyama, Y. Sekine,
Y. Tasiro, J. Arisawa, T. Fukuda, M. Honda,
H. Kato and N. Taniguchi

Mr. T. Kozaki and Miss R. Oyama jointed the laboratory, and Mrs. N. Ochiai moved to the library of the faculty of engineering. The current research activities of the laboratory are mainly concerned with corrosion of metallic materials used in nuclear industry, characterizations of iron rust components, development and improvement of hydrogen reservoir alloys, clarification of the mechanism of pitting corrosion, migration of noble metal fission products in UO_2, and radioactive waste management.

(1) Magnetite and nickel ferrite were synthesized by several methods and characterized by XRD, SEM, Mössbauer spectroscopy, and surface area measurements.

(2) The dissolution rates of magnetite were measured in aqueous solutions including two kinds of decontamination reagents, EDTA and $EDTA+N_2H_4$, to determine the mechanism of dissolution of magnetite with the decontamination reagents.

(3) Structural changes of the hydrogen storage materials caused by absorption and desorption of hydrogen were investigated by an acoustic emission method (AE). Changes in lattice parameters and Mössbauer spectra were studied as a function of absorption and desorption cycles of hydrogen. The process of pulverization caused by hydrogen absorption was characterized with measurements of the distribution of AE frequency and AE appearance time interval correlations. The process was divided into two steps

dependent on the process of hydrogen absorption ; the one AE is the first process of crack occurrence along the grain boundary of alloy and the other AE is the second process generated through the boundary. The AE frequency showed high values at the first step and changed to low values in the step of the second process.

(4) Pitting corrosion of iron was studied in buffered solutions by in-situ spectrum analysis of fluctuations of corrosion currents. Growth of pits was predicted by variation of the spectrum change of the current. The spectrum analysis method yielded the following results : the shape of the spectrum in the range from 10^0 to 10^{-3} Hz showed $f^n(-1 \leqq n \leqq 0)$ as the inclination after setting electrode potentials, and it changed from the shape of f^0 with an initial white spectrum with time in the passive region, but it stayed far from the white spectrum $f^n(-1 \leqq n \leqq -0.5)$ in the active and transpassive regions, spectra changed from white before pitting occurs with Cl^- ion addition ; We could predict the time when pitting starts.

(5) Pd is the most corrosive noble metal fission product against SiC in fuel kernel for high temperature gas-cooled reactors. To clarify the effects of the Pd on the fuel performance, the migration behavior of the Pd in an uranium dioxide pellet has been studied. Penetration profiles of the Pd in the pellet were obtained by an electron probe micro-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 the Pd, an evaluation of several migration processes are under way.

(6) One important phenomenon in fabrication of high level radioactive waste glass is the formation of metal and ceramic precipitates, which may affect stable operation, such as Joule heating of the melter and drainage of glass melt out of a nozzle. The redox state of iron in simulated waste glass is a promising indicator for the study of the precipitation. As a preliminary study, thin sim-

ulated waste glass was enclosed with an oxygen buffer such as metal/metal oxide powder and with CO_2 as the oxygen carrier in quartz glass tubes and heated for 7 days at temperatures of 723 and 1023 K. The amounts of Fe (II) and Fe (III) were determined by chemical analysis. Log {Fe (III)/Fe (II)} was found not to be in proportion to the oxygen potential. The complex relation of log {Fe (III)/Fe (II)} to the oxygen potential was discussed using the data of observations of the precipitates including Fe (III) and Fe (II) by SEM/EDS, and XRD.

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

(8) In basic research 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 thermodynamic data is discussed on the basis of the interlayer distance obtained by the XRD method.

(9) For purposes of safety analysis of nuclear waste disposal, the migration processes of fission products and actinides in geologic formation must be determined. 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

Cold Fusion Research in Hokkaido University; T. Mizuno, T. Akimoto and K. Azumi: Meeting of Synthetic Research of Cold Fusion Tokyo, Feb., 4, 1991

Migration Behavior of Uranium (VI) in Laboratory Scale Granite; K. Idemitsu, H. Furuya, Y. Inagaki and S. Sato: The Third

International Symposium on Advanced Nuclear Energy Research —Global Environment and Nuclear Energy,—, Mito, Ibaraki, March 13-15, 1991.

Volumetric Change and Helium Behavior in Irradiated Waste Glass; S. Sato: Yayoi Conference on Radioactive Waste Disposal and Scientific Basis, Nuclear Engineering Research Laboratory, Faculty of Engineering, University of Tokyo, March, 1991.

A Report on Waste Management '91 at Tucson; H. Ohashi: Seventh Regular Meeting of Group of Waste Reprocessing in Nuclear Reactor Commission of Japan Nuclear Industrial Committee. Tokyo, April 1991.

Geological Disposal and Properties of Waste Glass and Engineered Barriers; S. Sato: Lecture in Hokkaido Section of Atomic Energy Society of Japan, Faculty of Engineering, Hokkaido University, June, 1991.

Prospect and Present of Cold Fusion; T. Mizuno: The 9-th Seminar of Electrochemical Society of Hokkaido division, Ohtaki, June., 8-9, 1991.

An Approach by Corrosion Science to the Failure Mechanism of Nuclear Reactor Materials; H. Ohashi: Investigation Commission for Improvent of Reliance on Reactor Material; Meeting of Atomic Energy at Kansai District, Kobe, July, 1991.

Confirmation of Cold Fusion; T. Mizuno, T. Akimoto and K. Azumi: Meeting of Synthetic Research of Cold Fusion, Tokyo, July., 29, 1991.

Physical and Chemical Properties of Radioactive Waste Glass and Engineered Barriers; S. Sato: The Seventh Summer Seminar on Radioactive Waste Management, Radioactive Waste Management Group, Atomic Energy Society of Japan, Shikabe Royal Hotel, July 1991.

Confirmation of Cold Fusion; T. Mizuno, T. Akimoto and K. Azumi: Meeting of Synthetic Research of Cold Fusion, Atami, Aug., 29, 1991.

On the Cold Fusion; H. Ohashi: Lecture at Central Institute of

Radioisotope, Hokkaido Univ., Sapporo, Sept. 1991.

Spectrum of Current Fluctuation and Corrosion of Iron; T. Mizuno, Febrianto, M. Kitaichi and H. Ohashi: The Fall Meeting of Chemical Society of Japan, Sep., 23, 1991.

Change of Spectrum of Current Fluctuation during Pitting Corrosion for Iron; T. Mizuno, Febrianto, K. Yamazaki and H. Ohashi: The Fall Meeting of Chemical Society of Japan, Sep., 23, 1991.

Confirmation of the Fleischmann-Pons Effect (Cold Fusion); T. Mizuno: The Fourth Int. Symp., (Frontiers of Electrocatalysis) Sapporo, Sep., 20-21, 1991.

Diffusion Behaviour of Fe(III) Ions in Compacted Bentonite; Y. Sekine, T. Kozaki, S. Sato, H. Ohashi, T. Tamai, Z. Takada, T. Ohe and M. Tukamoto: Fall Meeting of the Atomic Energy Society of Japan, Oct., 1991.

Migration Behavior of Pd in Uranium Dioxide; M. Yoneyama, S. Sato, H. Ohashi, T. Ogawa, A. Ito and K. Fukuda: Fall Meeting of Atomic Energy Society Japan, Oct., 1991.

Redox-State of Iron in Simulated Radioactive Waste Glass; Y. Sugita, Y. Tashiro, S. Sato and H. Ohashi: Annual Meeting of Hokkaido-section of Atomic Energy Society of Japan, Dec., 1991.

ANALYTICAL CHEMISTRY LABORATORY

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

Students

A. Furusaki, M. Kudo, K. Ishizeki, M. Watanabe, A. Uchibo, K. Ohkita, C. Tabata and R. Segawa

Professor Furuichi was serving as the chairman of the Hokkaido Section of the Surface Finishing Society of Japan for the second year. Mr. Saeki, a former student of this laboratory who worked for Nisshin Steel Co., has jointed our group as research associate in April. Dr. Konno participated in The 42nd Meeting of The International Society for Electrochemistry at Montreux in August. Dr. Tamura jointed The 5th IBA Battery Materials Symposium at Sydney in November.

The research programs in our laboratory are:

(1) *Incorporation of impurity metal ions into electrolytic manganese dioxide (EMD)*

The incorporation of Pb^{2+} ions into EMD was studied and it was found that this ion is more largely incorporated than Cu^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+} ions examined before. The adsorption affinity of this ion for the surface of manganese dioxide was also investigated and a good correlation between the incorporation and adsorption was found. Mechanisms of incorporation were discussed in relation to the production of high purity EMD for battery use.

(2) *Ion-exchange adsorption affinity of Li^+ ions for manganese dioxide*

The ion-exchange adsorption behavior of Li^+ and other alkali metal ions on MnO_2 IC22 was studied. The results were similar to those obtained for MnO_2 IC12. The higher affinity of Li^+ than other ions at higher coverages was ascribed to its smaller charge density due to higher hydration, as it reduces suppression of ion exchange caused by lateral interactions between adsorbed ions.

(3) *Analysis of the ion-exchange properties of weak-acid type cation-exchange resin*

For a porous type ion-exchange resin (IRC-50), the ion exchange with alkali metal ions was examined. The ion-exchange behavior was analysed with the model considering two types of sites with different reactivities and lateral interactions between the interphase species. The reactivities of the respective sites were determined and it was concluded that one type of sites is in macropores and the other type of sites in micropores of the resin.

(4) *Formation of perovskite structure lanthanum chromium oxide films by electrodeposition*

A method to form perovskite structure lanthanum chromium oxide was further developed to substituted oxide systems, $La_{1-x}M_x CrO_3$ [M=Ca or Sr]. Precursor films to the oxides, $(LaOH)_{1-x}M_x CrO_4\ nH_2O$ [$x<0.1$ with Ca and $x \leqq 0.2$ with Sr], were formed on Ni, or stainless steels by the cathodic deposition, and the pyrolysis conditions to form $La_{1-x}M_xCrO_3$ films were surveyed. Further, formation and sintering of $La_{1-x}M_xCrO_3$ from precursors on metals are under investigation by laser irradiation.

(5) *Synthesis of perovskite structure lanthanum chromium oxides by a novel route*

A method to synthesize both A-site and B-site substituted perovskite structcre lanthanum chromium oxides, $(La_{1-x}A_x)(Cr_{1-y}B_y)O_3$ [A=Ca or Sr, B=Mn, Co and so on] was developed using Cr (VI) compounds as starting materials. This novel route enabled the perovskite structure oxide to be formed with lower energy consumption than conventional method. The formation mechanism was investigated by TG-DTA, XRD, IR, EPR, XPS, and chemical analysis. It was found that under a limited formation condition $LaCrO_4$ is formed as a single phase intermediate. The $LaCrO_4$ was found to be an exceptionally stable Cr (V) compound. Chemical and physical properties of the compound is under investigation.

(6) *Electrochemical formation of mixed oxide films on metals*

Cathodic reduction of NO_3^- ions was successfully applied to form gel like thin films on metals from metal nitrate solutions. The Al(III)-Y(III) mixed hydroxide films around 1 μm in thickness were formed on Ni and stainless steels, and they showed good performance as protective oxide coatings under oxidizing atmospheres at elevated temperatures. The process can be applied to form other mixed oxide flms such as Y doped ZrO_2, Ce_2O_3-CeO_2, and so on. A project to examine the detailed scheme of the film formation 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 effect of Nb or Ti doping on the corrosion resistance of the alloy was investigated at 80°C in air with different relative humidities by XPS and ellipsometry. The project is still continuing.

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

Generally the life time to the occurrence of breakaway oxidation of chromia forming Fe-Cr alloys is shorten by the presence of H_2O in the atmosphere. The roll of H_2O is not well known but if it affect to the life time, the nature of surface oxide film formed before breakaway must be different with p_{H_2O}. To study this subject, a new apparatus, with which specimens could be heated quickly with the rate of 40 K/s, was constructed and oxidation of Fe-Cr alloys were carried out at 1273 K in H_2O-O_2-N_2 or O_2-N_2 atmosphere up to 180s. It was found that the morphology, structure and composition of the surface oxide films change with p_{H_2O} by SEM, XRD and XPS.

Oral Presentations

Formation of A-Site Substituted Lanthanum Chromium Composite

Oxide Films by Electrodeposition ; M. Tokita, H. Konno and R. Furuichi : The 17th Meeting of the Hokkaido Sec. of Electrochem. Soc. Jpn., Jan., 1991.

Corrosion of Fe-Al-Si Alloys for Magnetic Head ; H. Konno, S. Matsugi, R. Furuichi, T. Nishimura and Y. Shimizu : The 26th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1991.

Characterization of the Ion-Exchange Behavior of a Weak-Acid Type Cation-Exchange Resin with Alkali Metal Ions ; M. Kudo, H. Tamura and R. Furuichi : The 1991 Winter Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. of Jpn., Feb. 1991.

Formation of Metal-Oxide Films on Metals by Electroreduction ; H. Konno and R. Furuichi : The 83rd Meeting of Surf. Finish. Soc. Jpn., Mar., 1991.

Ion-Exchange Behavior of Resin Carboxyl Groups with Alkali Metal Ions —Polyfunctionality and Lateral Interactions— ; H. Tamura, M. Kudo and R. Furuichi : The 61st Spring Meeting of Chem. Soc. of Jpn., Mar. 1991.

Composition of Oxide Films Formed on Fe-Al-Si Magnetic Alloys in Humid Air ; H. Konno, S. Matsugi, R. Furuichi and T. Nishimura : Corrosion '91, May, 1991.

Formation of Composite Oxide Films on Metals by Cathodic Deposition ; H. Konno : The 23th Seminar on Wet Process Techniques, May, 1991.

Analysis of Ion-Exchange Properties of Inorganic Exchangers ; H. Tamuta and R. Furuichi : The 52nd Symposium of Jpn. Soc. for Anal. Chem., May 1991.

Analysis of the Ion-exchange Adsorption Affinity of Alkali Metal Ions for Surface Hydroxyl Groups on Manganese Dioxide ; N. Katayama, H. Tamura and R. Furuichi : The 1991 Summer Meeting of Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., July 1991.

Electrochemical Formation of A-Site Substituted Perovskite-Type $La_{1-x}M_xCrO_3$ Oxide Coatings ; H. Konno, M. Tokita and R.

Furuichi: The 42nd Meeting of ISE, Aug., 1991.

Ion-Exchange Adsorption Affinity of Li^+ Ions for Surface Hydroxyl Groups on MnO_2; N. Katayama, H. Tamura and R. Furuichi: The 62nd Fall Meeting of Chem. Soc. Jpn., Sept. 1991.

Ion-Exchange Adsorption Properties of Co^{2+} Ions for Surface Hydroxyl Groups on Hematite; N. Katayama, H. Tamura and R. Furuichi: *ibid.*

Electrochemical Formation of the Oxide Coating Resistant to High Temperature Oxidation; H. Konno: The 22nd Meeting of the Technical Division on Functional Amorphous Plating of Surf. Finish. Soc. Jpn., Sep., 1991.

Formation of Lanthanum Chromium Composite Oxide by Thermal Deposition and Thermal Analysis of the Process; A. Furusaki, H. Konno and R. Furuichi: The 62nd Annual Fall Meeting of Chem. Soc. Jpn., Sep., 1991.

Alteration of the Surface Composition of Fe–Cr Alloys by Vaccum Annealing or Laser Irradiation; H. Konno, I. Saeki and R. Furuichi: The 38th Annual Symposium on Corrasion and Protection, Oct., 1991.

Polyfunctionality of Porous-Type Ion-Exchange Resin; H. Tamura, M. Kudo and R. Furuichi: The 40th Annual Meeting of Jpn. Soc. for Anal. Chem., Nov. 1991.

Mechanism of Incorporation of Impurity Metal Ions into EMD; H. Tamura, K. Ishizeki, M. Nagayama and R. Furuichi: The 5th IBA Battery Materials Symposium, Nov. 1991.

Formation of Protective Oxide Films by Electroreduction and Evaluation of the Oxidation Resistance at Elevated Temperatures; H. Konno: The 11th Meeting of the Technical Division on the Evaluation of Corrosion Resistance of Surface Treated Materials of Surf. Finish. Soc. Jpn., Dec., 1991.

ELECTROMETALLURGY LABORATORY

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

Students

Dr. K. Miura, T. Kumagai, H. Tanaka, M. Maeda,
Marusudi Wibowo, M. Kosaka, M. Noguchi,
K. Ogata, M. Takahashi, K. Nagata, A. Matsunaga,
H. Murakami and I. Yamazaki

Professor Ishikawa and Associate Professor Sasaki participated in the third Conference of Hokkaido University and University Science and Technology Beijing in Beijing, China, 9th–11th, September.

Dr. Notoya had a talk at the 7th Asia-Pacific Corrosion Control Conference in Beijing, China, 19th–23rd, August. He participated in the 180th Electrochemical Society Meeting in Phoenix, Arizona, U.S.A., 13th–17th, October.

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) 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.

(4) The corrosion resistance of various kinds of chromium-con-

taining alloys in sulfuric acids is being evaluated by electrochemical techniques.

(5) 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.

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

(7) Surface tarnishing and corrosion inhibition mechanisms of copper and copper alloys have been investigating with organic inhibitors by using electrochemical techniques and surface analysis method. Preventive measures for "Ant's nest" corrosion in copper tubings have also been attempted with anti-tarnishing surface treatments.

(8) 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

Production of Al_3Ti in Molten Salts Containing $TiCl_4$; T. Kumagai, S. Konda, T. Narita and T. Ishikawa: The 17th Hokkaido Section Meeting of Electrochem. Soc., Japan, Jan., 1991.

In situ Observation of p-Mercaptphenol Adsorbed on Gold by FTIR Spectroscopy; T. Sasaki and T. Ishikawa: *ibid.*, Jan., 1991.

In situ Observation of a Metal Surface by Infrared Reflection Absorption Spectroscopy; T. Sasaki and T. Ishikawa: The 26th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1991.

On the Corrosion Resistance of Copper and Copper Alloys; T. Notoya: Seminar on Maintenance Techniques for Heat Exchangers of Japan, March, 1991.

Effect of Surface Treatment with Organic Inhibitors on Ant's Nest Corrosion in Copper Tubes; T. Notoya and T. Ishikawa: The 61st Spring Meeting of Japan Chemical Society, March, 1991.

Production of Al Alloys Dispersing Al_3Ti Particles in Molten Chloride Salts; T. Kumagai, S. Konda, T. Sasaki, T. Narita and T. Ishikawa: The 58th Annual Meeting of Electrochem. Soc. Japan, Apr., 1991.

Reduction Characteristics of Chlorine Gas on Graphite Electrodes in Molten Chloride Salts; M. Maeda, S. Konda, T. Sasaki, T. Narita and T. Ishikawa: *ibid.*, Apr., 1991.

Decrease in Concentration of Oxygen Dissolved in a Tap Water by a Galvanic Cell; S. Konda, T. Sasaki, T. Narita and T. Ishikawa: *ibid.*, Apr., 1991.

In situ Infrared Spectroscopic Studies of Aromatic Thiols Adsorbed on Gold Polycrystallines; T. Sasaki and T. Ishikawa: *ibid.*, Apr., 1991.

Corrosion Prevention of Localized Corrosion in Copper Tubes by Anti-tarnishing Surface Treatments; T. Notoya and T. Ishikawa: Corrosion and Corrosion Prevention '91, May, 1991.

Effect of Pretreatment with Chromic Acid and Benzotriazole on Corrosion of Oxygen Free Copper and Phosphorus Bronze in Formic Acid and Sodium Formate Solutions; T. Notoya and T. Ishikawa: The '91 Hokkaido Section Spring Meeting of JIM, June, 1991.

Electrochemical Studies of Anti-corrosive Characteristics of Magnesium Alloys Containing Aluminum; T. Moriyasu, T. Sasaki and T. Ishikawa: *ibid.*. June, 1991.

Effect of Surface Pretreatment with Chromic Acid and Benzotriazole on Tarnishing of Copper and Copper Alloys; T. Notoya and T. Ishikawa: The 11th Meeting of Japan Rust Prevention Association, July, 1991.

Effect of Anti-tarnishing Pretreatment on a localized Corrosion in Copper Tubes; T. Notoya and T. Ishikawa: The 7th Asia-Pacific Corrosion Control Conference, Beijing, China, August, 1991.

In situ Studies of Thiols Adsorbed on Gold by FTIRRAS; T. Sasaki and T. Ishikawa: The third Conference of Hokkaido University and University Science and Technology Beijing, Sep., 1991.

Ant Nest Corrosion in Copper Tubing; T. Notoya and T. Ishikawa: The Electrochemical Society 180th Meeting, Phoenix, Arizona, U.S.A., Oct., 1991.

Solubility of Various Chlorides in Low Temperature Chloride Melts Containing $AlCl_3$; T. Matsutani, T. Sasaki, S. Konda and T. Ishikawa: The '91 Fall Meeting of the Electrochem. Soc. Japan, Oct., 1991.

Electrowinning of High-pure Metals by an Electrochemical Cycle in a Molten Salt System; M. Maeda, S. Konda, T. Sasaki and T. Ishikawa: The 23rd Symposium on Molten Salt Chemistry, Nov., 1991.

Dissolution Behavior of Titanium Tetrachloride in the Molten Salts of an eq. Molar NaCl-KCl Mixture; T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: *ibid.*, Nov., 1991.

Dissolution Behavior of $TiCl_4$ in High Temperature Chloride Melts: T. Kumagai, S. Konda, T. Sasaki and T. Ishikawa: The '91 Hokkaido Section Fall Meeting of JIM, Nov., 1991.

In situ Investigation of Electrode Surfaces by IRRAS; T. Sasaki and T. Ishikawa: *ibid.*, 1991.

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, Y. Ito, T. Ida, E. Umekawa,
M. Kamada, M. Kubota, S. Hayashi, T. Sasaki
and T. Yoshioka

Professor T. Narita was a former associate professor of Electrometallurgy Laboratory and at April in 1991 he was promoted to new professor of Composite Materials Processing and Evaluation Laboratory. Professor Narita attended The 5th International Congress on Non-Destructive Evaluation, held in Japan at June, 1991. Mr. Matsuura attended the International Conference on Grain Growth in Polycrystalline Materials, held in Italy at June, 1991. Professor Narita and Associate Professor Ito attended the 3rd Hokkaido University — University of Science and Technology Beizing, held in China at September, 1991, and then Professor Narita attended the 4th Japan-China Science and Technology Symposium.

The research programs in our laboratory are :

(1) Ceramic-metal joining

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 joining was investigated for development of SOFC.

(2) High-temperature sulfidation of alloys

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

(3) Ultrasonic micro-spectroscopy

Scanning acoustic microscope (HITACHI 1000S) was installed in our laboratory and is being utilized to measure the thermal residual stress of the ceramic-metal joint. The principle concept of the novel method is basing on the surface acoustic wave velocity and its change with stresses. This was further extended for simultaneous measurements of stress and surface distortion of the ceramic-metal joints and other composite materials.

(4) Discolouring process of zirconia ceramics

Zirconia ceramic was found to be degraded in accompanying with discolouring phenomena when it was joined to metals 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 size 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 plasuma assisted hot-pressing 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

Simultaneous Measurements of Stress and Distortion of Ceramic-Metal Joints-Thermal Cycling Tests of Silicon Nitride Ceramic-Nickel joints; T. Narita and T. Ishikawa: The 23rd Symposium on Stress and Strain, Jan., 1991.

Formation of Al_3Ti from Fused Salts Containing Titanium Tetrachloride; T. Kumagai, S. Konda, T. Narita and T. Ishikawa: The 17th Meeting of the Hokkaido Sec. of Electrochem. Soc. of Jpn., Jan., 1991.

Columnur Grain Growth of Gamma Phase of Cast Iron; K. Matsuura and Y. Ito: Seminar at Hokkaido Section of Iron and Steel Soc. Jpn, Jan., 1991.

High Temperature Sulfidation of Austenitic Stainless Steels; S. Kawamori and T. Narita: The 26th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1991.

Effect of High-Temperature Oxidation on Strength of Si_3N_4-Metal Joints; K. Miura, T. Narita and T. Ishikawa: The 180th Annual Meeting of JIM, Apr., 1991.

Discolouring Phenomena of ZrO_2 Ceramics Joined to Metals; T. Mitsueda and T. Narita: *ibid.*, Apr., 1991.

Simultaneous Measurements of Stress and Distortion Using Scanning Acoustic Microscopy —Principle and Application—; T. Narita and T. Ishikawa: *ibid.*, Apr., 1991.

Evaluation of the Surface Damaged ZrO_2 Using Scanning Acoustic Microscope; Y. Shibata, T. Narita and T. Ishikawa: *ibid.*, Apr., 1991.

Sulfidation Behavior of Stainless Steels in Low Sulfur Pressures; S. Kawamori and T. Narita: *ibid.*, Apr., 1991.

Computer Simulation of Three Dimensional Grain Size Distribution; K. Matsuura and Y. Ito: *ibid.*, Apr., 1991.

Electrolysis from Fused Salt; T. Kumagai, T. Narita and T. Ishikawa: The 58th Annual Meeting of Electrochem. Soc., Jpn, Apr., 1991.

Reduction Process of Chloride Gas on the Graphite Electrode in Fused Chloride Melts; M. Maeda, S. Konda, T. Sasaki, T. Narita and T. Ishikawa: *ibid.*, Apr., 1991.

Reduction of Oxygen Dissolved in Tap Water by the Cell Reaction Method; S. Konda, T. Sasaki, T. Narita and T. Ishikawa: *ibid.*, Apr., 1991.

Application of Scanning Acoustic Microscopy to Ceramic-Metal

Interface; T. Narita: IRJSIS Seminar, May, 1991.

Simultaneous Measurements of Stress and Strain of the Ceramic/metal Joint by Ultrasonic Micro-Spectroscopy; T. Narita, I. Ishikawa and T. Ishikawa: The 5th International Symposium on NDE of Materials, May, 1991.

Effect of Grain Size Distribution on Grain Growth; K. Matsuura and Y. Ito: International Conference on Grain Growth in Polycrystalline Materials, June, 1991.

Grain Boundary Sulfidation of Stainless Steels; S. Kawamori and T. Narita: The Meeting of Hokkaido Section of JIM, June, 1991.

Reactivity of ZrO_2 Ceramics to Materials; T. Mitsueda, T. Narita and T. Ishikawa: ibid., June, 1991.

Computer Analysis of Stress and Strain of Ceramic-Metal Joints with FEM; M. Noguchi and T. Narita: *ibid.*, June, 1991.

Effect of MnS on the 1st Recrystallization of the Martensitic Low Carbon Steel; K. Taumi and Y. Ito: *ibid.*, June, 1991,

Diffusion Bonding of the High Carbon Steel and SUS310S Steel; N. Yonezawa, K. Yamazaki and Y. Ito: *ibid.*, June, 1991.

Computer Simulation of the Thermal Residual Stress of the Ceramic-Metal Joints; Seminar on FEM Application . July, 1991.

On the Ultrasonic Microspectroscopy; T. Narita: Seminar of Hokkaido Section of the Surface Finishing Soc., Aug., 1991.

Joining of the Fully Stabilized Zirconia Ceramics to Metals Using Ag-Cu-Ti Solder and Ni Interlayer; T. Narita, Y. Ito and T. Mitsueda: The 3rd Hokkaido Univ. — Univ. of Science and Technology Beizing, Sep., 1991.

Joining of Fully Stabilized Zirconia to Metals Using Active Metal Solder; T. Narita and T. Mitsueda: The 4th Japan-China Science and Technology Symposium, Sep., 1991.

Some Aspects on the Ceramic-Metal Joinings; T. Narita: Lecture at THJR, Sep., 1991.

Research and Development of the Ceramic-Metal Joints; T. Narita: Lecture at Meeting of the JPCC, Sep., 1991.

Properties of the Degraded Zirconia Ceramics; T. Mitsueda and

T. Narita: The 109th Annual Meeting of JIM, Oct., 1991.

Computer Simulation of the Internal Sulfidation Phenomena; S. Kawamori and T. Narita: *ibid.*, Oct., 1991.

Elastic-Plastic Analysis of the Ceramic-Metal Joint with FEM; T. Narita and M. Noguchi: *ibid.*, Oct., 1991.

Application of Ultrasonic Microspectrscopy to Materials Characterization; T. Narita: Lecture at Hitachi NDE Seminar, Nov., 1991.

Measurement of Minute Corrosion of Metal Thin Films by a Quartz Crystal Microbalance

Masahiro Seo

Bunseki, No. 4, 284-286 (1991)

Quartz crystal microbalance (QCM), which is capable of detecting a trace amount of mass changes in the magnitude of 10^{-9} g cm^{-2} from the changes of resonant frequency, is useful for monitoring minute corrosion of metal thin films. This article dealt with the application of QCM to adsorption of water molecules and atmospheric corrosion of metal thin films. The typical QCM results of adsorption isotherm of water molecules and atmospheric corrosion kinetics were introduced. (Japanese)

Comparison of Stress Corrosion Cracking Susceptibility of Austenitic and Ferritic Stainless Steels in Small Punch Testing

T. Misawa, T. Ohtsuka, M. Seo and M. Saito

J. Nuclear Materials, **179-181,** 611-614 (1991)

The small punch (SP) test technique combined with electrochemical measurements for irradiated miniaturized specimens has been developed to evaluate the resistance to stress corrosion cracking (SCC) and corrosion of fusion reactor structural steels in water-cooled environment under irradiation. An apparatus developed for SP-SCC testing using small specimens in a high temperature and high pressure aqueous solution under applied potential conditions was successully demonstrated in the comparison of SCC susceptibility between Type 304 austenitic and HT-9 ferritic stainless steels. The SP fracture energies necessary for SCC initiation measured from the load versus deflection curves were obtained as a function of the applied potential. The occurrence of susceptibility zones to SCC was observed at the corrosion potential and transpassive regions of sensitized Type 304 steel. Surface films were examined by scanning electron mocroscope, Auger electron spectroscopy and laser Raman spectroscopy. The relationship between the nature of surface films and SCC susceptibility is discussed.
(English)

Effect of Temperature and Dissolved Oxygen on the Corrosion Behavior of Carbon Steel in high-Temperature Water

K. Mabuchi, Y. Horii, H. Takahashi and M. Nagayama

Corrosion **47**, 500–508 (1991)

The corrosion behavior of carbon steel in high-temperature water, and the structure and composition of the oxide film were examined as functions of dissolved oxygen concentration (DO), temperature (T), and corrosion time (t). The total amount of iron corroded (W_T) was differentiated into the amounts of iron ions in the oxide (W_F) and dissolved into the water (W_D). The total rate of corrosion (r_T), the rate of iron dissolution (r_D), and the rate of accumulation of iron in the oxide (r_F) were obtained by differentiating the time variations in W_T, W_F, and W_D.

The structure and composition of the oxide film were examined by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission and scanning electron microscopy. In general, r_T increases with increasing DO and T, r_D shows T- and DO-dependent minimum, and there is serious localized corrosion at high DO above 500 ppb. Oxide films consist of magnetite except at $T=60°C$, $DO=50$ to 200 ppb where a thin layer of hydrous ferric oxide is formed. At $DO=500$ ppb, the outermost part of the magnetite changes into γ-Fe_2O_3, and above $DO=1.0$ ppm, appreciable amounts of α-Fe_2O_3 cover the magnetite oxide layer. The r_T and r_D values are not related to the presence of γFe_2O_3 or Fe_3O_4 in the surface structure of the oxide, but clearly decrease as the OH^-/Fe mole ratio at the oxide surface increases. The mechanism determining the corrosion rate is discussed. (English)

Effect of surface Pretreatment on Ant's Nest Corrosion in Copper Tubing

Takenori Notoya

Journal of the Japan Copper and Brass Research
Association Vol. 30 p. 37 (1991)

Copper tubes are widely used in refrigerating and air-conditioning units. An usual mode of corrosion of copper tubes has been detected early in service and even at the leakage tests after manufacture. The morphology of this corrosion is similar to an "ant nest" when viewed in cross section. The pinholes penetrating the copper walls are generally difficult to detect by the naked eye. However, when observed with an optical microscope, cross, section of corroded segments are characterized by complicated microscopic caverns connected by a network of tunnels containing porous copper oxide in directional pits. This localized ant nest corrosion is believed to be caused by a small amount of carboxylic acid which is produced by the hydrolysis of chlorohydrocarbons used as detergent. The present paper deals with the comparison of localized corrosion in as-received copper tubes with that in surface treated ones. The surface treatment given was of two types: (i) anti-tarnishing pretreatment with nine different organic corrosion inhibitors, and (ii) physical vapour deposition of five different metals on the copper tube surface. Exposure tests were performed to evaluate the surface treatment using oxygen free high purity copper and phosphorous deoxidized copper tubes. The pretreated copper tubes were placed in a humid atmosphere over water containing a small amount of formic acid, or acetic acid, in an air-tight glass vessel at room temperature for 30 days. Almost all the surface of the unpretreated copper tube was tarnished, while the pretreated copper tubes with the organic inhibitors, particularly benzotriazole, maintained metallic lustre in all areas except their top ends. No corrosion was found in the shiny untarnished area

of the treated tube surface when viewed under an optical microscope. It was found that a thin metalic coating of Zn, Ni, Ag, Sn, or Pb provided by physical vapour deposition, gave little protection against the localized corrosion.

It could be concluded that the anti-tarnishing pretreatment gave some protection to the copper tubes and was effective in preventing tarnishing of their surfaces. The top ends of the treated copper tubes however show a greenish-blue colour of corrosion products after 30 day exposure because of an edge effect, and were severely affected by localized corrosion. Plausible reaction pathways of the corrosion are also presented. (Japanese)

Effect of Anti-Tarnishing Pretreatment on Localized Corrosion in Copper Tubes

Takenori Notoya

Proceedings of the 7th Asian-Pacific Corrosion
Control Conference Volume 1 p. 194 (1991)

A pretreatment of copper tubes with nine different organic inhibitors has been evaluated for effectiveness in preventing an unusual type of localized corrosion (ant-nest corrosion) in a humid atmosphere containing a small amount of formic acid. The pretreatment was carried out by immersion of copper tubes in an aqueous solution or methanol with the organic inhibitor at 60°C for 30 min. The inhibitive power of the pretreatment was assessed by the extent of metallic lustre maintained on the copper tube surfaces after 30 days exposure to the humid acidic environments in an air-tight bottle at room temperature. The cross section of copper tubes was examined by an optical microscope. The benzotrizole pretreatment has proven to be the most beneficial among the inhibitors in inhibiting tarnishing of the copper surface. Because of an edge effect, however, the top edge of both untreated and pretreated copper tubes was severely affected by the localized corrosion. (English)

Localized Corrosion in Copper Tubes and Its Inhibition by Surface Pretreatment with 2-Undecylimidazole

Takenori Notoya

Memoirs of the Faculty of Engineering, Hokkaido
University, Vol. XVIII, No. 2 (No. **79**)
p. 15 February (1991)

Localized corrosion protection in copper tubes was evaluated in an exposure test. This particular method can be achieved by pretreating the copper tubes with four different inhibitor solutions. The untreated and pretreated copper tubes were exposed to a humid atmosphere over an acid solution containing a small amount of carboxylic acid (such as formic acid, acetic acid or propionic acid) in an airtight glass vessel for 40 days. 2-Undecylimidazole showed excellent performance and proved superior to benzotriazole. Pretreatment with chromic acid and potassium dichromate hardly any protection against localized corrosion in copper tubes. Optical micrographs showing cross sections of the localized corrosion with and without these inhibitor pretreatments are presented. (English)

Corrosion Inhibition of Copper with Benzotriazole and Tolyltriazole in a 3% NaCl Solution

Guo-ding Zhou, Zichuan Ma, Ruting Tong
and Takenori Notoya

Bulletin of Electrochemistry 7 (2)
February 1991, pp. 60–63

Impedance measurements of copper electrodes in 3% NaCl solutions (pH 6) with additions of benzotriazole (BTA) and/or tolyltriazole (TTA) were made. Corrosion inhibition of copper after 15 min. immersion is stronger with BTA than with TTA for concentrations below 10 ppm, and stronger with TTA at concentrations above 20 ppm. The Cu–BTA film formation is more rapid than the Cu–TTA film formation. A combination of BTA and TTA gives a synergistic effect, and the optimum ratio with 40 ppm inhibitor is 30 ppm TTA+10 ppm BTA. (English)

Localized Corrosion in Copper Tubes and the Effect of Anti-Tarnishing Pretreatment

T. Notoya

Journal of Materials Science Letters **10** (1991) 389-391

Copper tubes are widely used in refrigerating and air-conditioning units. Localized corrosion of copper tubes has been detected early in service or even at the leakage tests after manufacture. The morphology of this corrosion is smilar to an "ant's nest" when viewed in cross-section. To prevent this corrosion the comparison of the localized corrosion in as-received copper tubes with that in benzotriazole treated copper tubes under a simulated condition. Benzotriazole-treated and untreated copper tubes were exposed to a humid atmosphere over formic acid for 1 month. The untreated copper tubes were tarnished and affected by localized corrosion. No corrosion was found in the shiny untarnished area of the treated copper surfaces except a top end of copper tubes. The top ends were severely affected by localized corrosion. The pretreatment gave considerable protection to the copper tubes and was effective in preventing tarnishing of their surface except the top ends. (English)

On the Corrosion Resistance of Copper and Copper Alloys

Takenori Notoya

Seminar Text on Maintenance Techniques for Heat
Exchangers: Basics and Topics p. 43 (1991)

The performance of copper and copper alloys is explained in the light of their nobility and protective film formation. The standard electrode potential and corrosion potentials of copper in different media are presented as compared with other metals. The corrosion resistance of principal copper alloys in service environments is determined by the nature of corrosion product films formed on the alloys. The chemical composition of the protective films on copper, aluminum brass, cupronickel and anti-pollution bronze is described. (Japanese)

Alkoxid-CVD Metal Oxide Surface Coating on Aluminum and Improvement Effect on Pitting Corrosion Resistance

T. Sakamoto, M. Seo, N. Sato, F. Jitoh,
M. Nabae and S. Furuya

J. Japan Institute Light Metals, **41**, 522–527 (1991)

Both the titanium oxide, TiO_2 and chromium oxide, Cr_2O_3 were deposited on aluminum substrate with alkoxid-CVD to improve the pitting corrosion resistance in neutral aqueous solution. Titanium tetraisopropoxide, $Ti(C_3H_7O)_4$ and chromium acetylacetonate, $Cr(C_5H_7O_2)_3$ were employed as evaporation sources for TiO_2 and Cr_2O_3, respectively. The deposition of oxides was performed at a deposition rate of about 60 nm h^{-1} under controlled mass flow rates (200 sccm and 500 sccm) of nitrogen carrier gas at different substrate temperatures (373 K to 573 K for TiO_2 and 703 K for Cr_2O_3), and at different evaporation source temperatures (298 K and 343 K for TiO_2 and 433 K and 513 K for CrO_3). Particularly, for the deposition of Cr_2O_3, water vapor at 353 K was added to nitrogen carrier gas to promote the deposition. The Auger analysis in depth indicated that aluminum of oxidation state is present in the interface layer between deposited oxide and aluminum substrate for both oxides. Furthermore, the ellipsometrical results suggested that the deposited oxides were amorphous. It was found that the average pitting potential of aluminum in pH 8.4 boric-borate solution containing 10^{-2} mol dm^{-3} Cl^- ions increased by 1.5 V due to the surface coating of both oxides with thickness of 40 nm. (Japanese)

Formation Mechanism of Porous Anodic Oxide Films on an Aluminum Die-Casting Alloy

Keiichi Watanabe, H. Takahashi, Ryusaburo Furuichi
and Masahiro Seo

Proc. of 7th Asia Pacific Corros, Control Conf.,
Vol. 2, 995–1000 (1991)

A commercial aluminum die-casting alloy, ADC12 (85.5Al–10.7 Si–2.1 Cu–Fe–Mn–Zn–Ni–Sn) was anodized galvanostatically in a sulfuric acid solution to examine the formation behavior of porous anodic oxide films by potential measurements, chemical analyses, evolved gas volume measurements, X ray diffraction measurements and electron microscopy. The results were compared with those from several Al–Si–Cu ternary alloys prepared by casting and rapid solidification.

During anodizing, the anode potential, E_a, increased with time, t_a, to a steady value, E_a^*. The value of E_a^* for ADC12 was similar to that for Al–10.7 Si–3 Cu rapidly solidified alloy. The high E_a^* value for ADC12 was found to be either due to the high Si- and moderate Cu-content, or the development of eutectic structure formed by the relatively high solidification rate of the specimen. ADC12 showed a high partial current for gas evolution and low partial current for film formation, and film dissolution. The behavior was correlated with the effects by trace alloying elements in addition to Si and Cu.

Electron microscopy showed that films formed on ADC12 have non-uniform thicknesses, and that the average thickness is relatively low. The non-uniformity of film thickness was attributed to the concentration of current into sites where α-aluminum phase had developed. The small average thickness was due to the low film formation rate, which was caused by the high partial current for gas evolution. (English)

Electron Microscopic Study of Anodic Oxide Films Formed on Aluminum with Thermal Oxidation

Hideaki Takahashi, Chiko Ikegami, Masahiro Seo and Ryusaburo Furuichi

J. Electron Microsc., **40,** 101–109 (1991)

The effects of thermal oxidation on the formation of barrier-type oxide films on aluminum were investigated by electron microscopy, gravimetry, and chemical analysis. Highly pure aluminum specimens were heated in air at 773–873 K for 1–24 hr, and then anodized in a neutral borate solution at 353 K with a constant current density of 50 A/m^2. Thermal oxide films were found to have a terminal thickness of ca. 30 nm after long heating periods, and to have a crystalline structure of γ-alumina. During anodizing, the rate of increase in the anode potential, E_a, for heat-treated specimens was twice as high as that for unheated specimens. The formation efficiency of anodic oxide films was 0.80 for heated specimens and 0.72 for unheated specimens. Anodic oxide film formed on heated specimens was a single including γ-alumina, and had a low thickness/E_a ratio of 0.77 nm/V. At high E_a, amorphous oxide islands were formed in the anodic oxide layer through the local breakdown of the crystalline oxide. (English)

The Effect of Heat Treatment of ADC 12 Aluminum Die Casting Alloy on the Formation of Anodic Oxide films in a Sulfuric Acid Solution

Keiichi Watanabe, Hideaki Takahashi, Ryusaburo Furuichi and Masahiro Seo

J. Metal Finishing Soc. Jpn., **42,** 933–940 (1991)

ADC 12 aluminium die casting alloy was heat-treated for various periods, t_h, at different temperatures, T_h, and anodized in 10 wt% sulfuric acid solution at 20°C by applying a constant current density, i_a, of 100 A/m^2. The film formation behavior and film properties were examined as fuctions of T_h, t_h and the abrasion thickness, X, of specimens by scanning electron microscopy (SEM), chemical analysis, and diffuse reflectance spectroscopy (DRS).

The steady value of anode potential, E_a*, was found to decrease with increasing T_h, t_h, and X. The ratio of dissolution current to i_a decreased with T_h and t_h, and was independent of X. Oxide films formed after anodizing for 40 min showed thickness differences on all specimens, and the variation in film thickness decreased with increasing T_h, t_h, and X. The value of average film thickness, δ, increased with T_h, t_h, and X and this expected to be due to an contribution of oxygen gas evolutions. DRS showed that the degree of film coloration decreases with increasing T_h and X.

The film formation mechanism is discussed with reference to structural change in the metal substrate due to the heat treatment. (Japanese)

Improving the Oxidation Resistance of Alloys by Surface Treatment with Active Elements

H. Konno and R. Furuichi

J. Surface Finish. Soc. Japan, **42,** 193 (1991)

Effect of active elements on the high temperature oxidation of heat resistant alloys, and various surface finishing methods using active elements were reviewed. The electrochemical techniques developed by authors to form oxide film containing active elements on metals were introduced with the results of oxidation tests. (Japanese)

Electrochemical Formation of the Oxide Coatings Resistant to High Temperature Oxidation

H. Konno

AMORPHOUS PLATING (Bulletin of the Technical
Division on Functional Amorphous Plating of Surf.
Finish. Soc. Jpn.), No. 22, p. 8-16 (1991)

Three types of electrochemical technique to form oxide films on metals were introduced. Composite oxyhydroxide films containing active elements and Cr or Al ions are formed by cathodic polarization of metals in aqueous solutions. By heating the films, they can be converted to oxide coatings resistant to high temperature oxidation. Results of oxidation tests above 900°C were also reported. (Japanese)

On the Inhibiting Materials Against Electrodeposition of Gallium in Bayer Liquor

Takeshi Toyoda, Masayuki Shiobara,
Takeshi Sasaki and Tatsuo Ishikawa

Bulletin of Faculty of the Engineering Hokkaido
University No. 155 (1991) 29

In order to identify the materials inhibiting electrodeposition of gallium in Bayer liquor, the electrolysis with gallium electrode was carried out in alkaline sodium aluminate solutions with additives of co-exising materials in Bayer liquor, and the dependency of current efficiency on the quantity of the additives was investigated.

Vanadium, silicon, and iron retarded the electrodeposition, but only in a much higher concentration range than those in Bayer liquor as treated by cooling. On the other hand, humic acid of 200 ppm, much lower than that in Bayer liquor, severly depressed electrodeposition. The results suggest that the humic compounds remaining in bayer liquor under cooling treatments are mainly responsible for low current efficiency in gallium deposition.

The attempt to remove the compounds from Bayer liquor was conducted by preelectrolysis followed by cooling reatments.

A considerable amount of fumic compounds was taken away by those treatments, but the current efficiency of gallium deposition decreased. It is probably due to the dissolution of gallium through some redox cycles caused by low molecular weight degradation products from humic compounds. The dissolution can also be accelerated by the concentration reduction of poisoning organic compounds. (Japanese)

Growth Behavior of Manganese-Metallized Layer on Silicon-Nitride Ceramics

Toshiyuki Takashima, Tsuyoshi Yamamoto
and Toshio Narita

J. Ceramic Soc. of Japan 99 [4], (1991), 324-328

The initial stage growth of a metallized layer of silicon-nitride ceramics was investigated by the vapor-diffusion method. The metallization was carried out using manganese powder as a vapor source under a dynamic vacuum condition from 1073 to 1273 K up to 129.6 ks. The metallization process was found to be divided into two reaction stages. At the initial stage a two layer structure was found; the surface layer of Mn_6Si and alpha-Mn(Si), and the bottom layer of $MnSiN_2$ and oxide additives. The thickness of the bottom layer increased rapidly at the onset of the initial stage. This change in layer thickness is due to the reaction of Si_3N_4 ceramics with manganese gas molecules supplied directly through opening and pores in the growing surface layers. After the initial transition period, the surface layer became compact, and a middle layer, a mixture of alpha-Mn(Si), Mn_6Si and oxide additives, was newly formed by decomposition of the bottom layer. Consequently, the thickness of the bottom layer decreased. Thereafter, it remained almost constant at 6.0 μm at 1173 K, 4.8 μm at 1223 K and 4.0 μm at 1273 K. Under steady state condition, it was found that the growth of the surface layer and bottom plus middle layer obeyed the parabolic rate law, respectively. (Japanese)

Effect of Grain Size Distribution on Grain Growth

Kiyotaka Matsuura and Youichi Itoh

Proc. International Conference on Grain Growth
in Polycrystalline Materials (June 1991,
Rome Italy), p. 23

The dominant parameter which controls the grain growth in a materials has been said to be temperature. However, the grain size distribution should also influence the growth rate, because the driving force of the grain boundary movement is the size difference between the adjacent grains. In this work, this effect on the growth rate was investigated by means of a computer simulation.

The results showed that the difference in the initial grain size distribution brought about the different behavior in the increasing process of the mean grain size, in spite of the same initial mean size and the same rate constant. The grain size distribution changed during the process, although it gradually converged on the steady state distribution which was independent of the initial distribution.

The growth rate dD/dt was able to be summarized as follows.

$$dD/dt = k(154Va - 5.76Ku - 11.4)/D^{1.2}$$

where, Va is the variation coefficient and Ku is the kurtosis of the grain size distribution. (English)

Estimation of Three-dimensional Grain Size Distribution in Polycrystalline Materials

Kiyotaka Matsuura and Youichi Itoh

Mater. Trans. JIM, 32 (1991), No. 11, p. 1034

A new method has been proposed for the estimation of the three-dimensional grain size distribution from the two-dimensional distribution measured on the cross section of polycrystalline material. In this method, twelve types of polyhedra were employed as the grain models. The distributions of the cross-sectional diameters of the individual polyhedra were expressed as probability density functions. On the basis of the functions for each polyhedron, the supposed grain size distribution on the cross section of the material was calculated, and it was compared with the measured one. The comparison was repeated until the agreement between the both distributions. By operating this two-dimensional distribution reversely, the three-dimensional grain size distribution was estimated.

The distribution of the vertex number of polygon-shaped grains on the cross section and that of the face number of polyhedron-shaped grains in three dimensions were calculated from the obtained results and were compared with the measured distributions. There was a good agreement between these distributions. (English)

Analysis of Effect of Grain Size Distribution on Grain Growth by Computer Simulation

Kiyotaka Matsuura and Youichi Itoh

Trans. ISIJ International, Vol. 31, (1991), No. 4, p. 366

The geometrical features of twelve kinds of polyhedrons were investigated, and the results were applied to the relationship between the grain shape and the size. Taking account of grain size and shape distribution, an expression for grain growth was proposed.

The expression was used to investigate the effect of the grain size distribution on the growth rate. It was found that the growth rate increased with increasing variation coefficient and with decreasing kurtosis. It was also found that growth exponent n was 2.2 during the steady growth. (English)

Measurements of Surface Acoustic Wave Propagation Velocity of Partially Stabilized Zirconia Joined to Metals

Toshio Narita and Tatsuo Ishikawa

J. Japan Inst. Metals, Vol. 55, No. 1 (1991), pp. 67-71

Using a reflection-type acoustic microscope, surface acoustic wave (SAW) velocities were measured with a frequency of 500 MHz on the partially stabilized zirconia (PSZ) ceramics itself as well as those jointed to nickel-Kovar alloy, with and without external stresses.

The relationship between SAW velocities (V_R, m/s) and tension stresses (σ, MPa) was given by the equation; $V_R = -0.21\sigma + 3270$. With this relationship, SAW velocities measured on the ceramic surface of the joint were transformed into stress and its distribution.

For the joint as-bonded, the largest tension stress of ca. 1 GPa was observed at the metal/ceramic interface and then it decreased rapidly far from the interface. With applying external load, the stress at the interface was unchanged, whereas the stress gradient tended to be steeper. After broken down the joint, a flat distribution was observed for the ceramic surface detached from the metal, showing residual stress free.

It was proposed that an acoustic microscope equipped with a minute loading unit shows considerable promise for non-destructive and localized evaluation of stress and its distribution on the ceramic surface, with and without external stresses. (Japanese)

XPS Study of the MnO_2 Electrode in Borate Solution During the Discharge Process

B. A. Lopez de Mishima. Toshiaki Ohtsuka,
Hidetaka Konno and Norio Sato

Electrochim. Acta, **36**, 1485 (1991)

The thin hydrous manganese oxide electrodeposited on gold has been studied using X-ray Photoelectron Spectroscopy (XPS). The oxygen 1s spectrum changes during the cathodic discharge process and can be deconvoluted into three components: Mn=O, Mn-OH or $Mn-OH_2$ and water adsorbed.

The surface composition of the film, $MnO_x(OH)_y(OH_2)_z$, has been described according to the O 1s spectrum analysis. The x and $y+z$ values were calculated from the I_o/I_m ratio peak intensities. The oxidation number of Mn has been calculated at different potentials during the manganese oxide reduction. These values indicate that MnO_2 is reduced to Mn(III) in borate solutions at pH 9.2. (English)

Codeposition of Impurity Metal Ions in Electrolytic Manganese Dioxide (EMD)

H. Tamura, K. Ishizeki, M. Nagayama
and R. Furuichi

Progress in Batteries and Battery Materials,
10, 192-199 (1991)

To study the mechanism of incorporation of impurity metal ions into MnO_2 during electrolytic preparation, the amounts of incorporated ions were measured as a function of metal ion concentrations and current densities. The results are summarized as

1. Incorporation of metal ion impurities in EMD increases with their concentration in solution.
2. The amounts of incorporated metal ions are in the order : $Fe^{3+} \gg Cu^{2+} > Co^{2+} > Ni^{2+}$
   The Fe^{2+} was completely oxidized to Fe^{3+} during the preparation of EMD
3. With increasing anodic current density, the amount of incorporated Fe^{3+} decreases, but incorporation of divalent metal ions increases.
4. The effects of the kind of metal ions and their concentrations in solution on the incorporation can be explained by considering that the incorporation occurs through the ion exchange of metal ions with protons of acid hydroxyl sites on MnO_2.
5. The effect of anodic current density on the metal ion incorporation can be explained in terms of either an increase in the specific surface area of EMD or an increase in electrostatic repulsion forces exerted by the anode. (English)

Characterization of the Ion-exchange Properties of Surface Hydroxyl Groups on Metal Oxides

H. Tamura and R. Furuichi

Bunseki Kagaku, **40**, 635-640 (1991)

The extent of cation and anion exchange on sparingly soluble metal oxide was measured by titration. Anion exchange was predominant at lower pH, and cation exchange at higher pH. Ion exchange occurs through an acid-base dissociation of the surface hydroxyl groups on the oxides followed by electrostatic adsorption of ions on the formed charged sites. The equilibrium conditions of the exchanges were derived by considering a suppresion of the ion exchange due to electrostatic repulsion between the adsorbed ions, $K_a^o = K_a \exp(A_a \theta_a)$, $K_b^o = K_b \exp(A_b \theta_b)$, where K_a^o and K_b^o are the intrinsic equilibrium constants, K_a and K_b are the concentration ratios at equilibrium, A_a and A_b are the suppression constants, and θ_a and θ_b are the coverages of the exchanged acid and base hydroxyl sites. The K_a^o and K_b^o values included in the equilibrium equations were determined by multiparametric curve-fitting. The parameter values for an oxide sample are specific; these values can be used to characterize the ion-exchange properties of oxide samples. The K_a^o values increased in the order Fe_3O_4, TiO_2, and MnO_2; the order of the K_b^o values was opposite. The different acidities and basicties of oxide samples could be explained in terms of the different positive charge densities of the lattice metal ions. The charge density increases with increasing valency and decreasing radius of the ions; the order of the density is $Fe^{2.7+} < Ti^{4+} < Mn^{4+}$. The larger positive charge densities promote the release of protons from adjacent hydroxyl groups (increase in acidity), and suppress the uptake of protons on the hydroxyl groups (decrease in basicity). (Japanese)

Ion Excharge of Na^+ with Resin Carboxylic Protons

Hiroki Tamura, Tatsuya Oda
and Ryusaburo Furuichi

Anal. Chim. Acta, **244,** 275-280 (1991)

The degree of exchange of Na^+ with resin carboxylic protons as a function of pH was measured by titration. The ion-exchange behaviour was characterized with a model in which the assumptions were made that resin has two types of carboxylic sites with different reactivities and the reactivity of each site decreases steadily as the extent of the excharge increases. The equilibrium conditions derived for the exchange reactions are expressed by a concentration ratio term and an exponential term for the coverage of the exchanged site, analogous to the Frumkin isotherm. The constants included in the model were determined by multiparametric curve-fitting. Fitting with other models were also attempted. It was found that the proposed model provides the best description of the experimental data. (English)

Migration Behavior of Uranium (VI) in Laboratory Scale Granite

K. Idemitsu, H. Furuya, Y. Inagaki and S. Sato

Proc. the Third International Symposium on Advanced
Nuclear Energy Research —Global Environment
and Nuclear Energy—, p. 207-211.
Mito, Ibaraki Japan (1991)

To study migration behavior of uranium (VI) through granite, column migration experiments were carried out in pH range 3.0 to 10.5.

Powder and wafer specimens of granite taken from India mine in middle Japan were used in this experiment. Concentrations of iodine and uranium (VI) of tracer solutions were 10 nM and 4.8 μM respectively. Sodium carbonate was also added into the trace solution up to 3 nM, usually 0.3 mM. Tracer solutions including iodine or uranium (VI) were passed through either column filled with powder, 32 to 60 mesh, or wafer specimen. Column for powder is 5 mm in diameter and 65 mm in length and wafer is 25 mm in diameter and 5 mm in length. Flow rates were approximately 0.15×10^{-6} m^3/h. Effluents were automatically collected by a fraction collector for subsequent analysis.

The migration of iodine was not retarded in all pH range of these experiments. The migration of uranium (VI) was retarded by a factor of 10 to 20. The maximum retardation was observed around neutrality of pH value.

The break-through curves were analyzed by a method which takes into account adsorption on surface of rock and diffusion into rock matrix but no dispersion. Diffusion of uranium (VI) and iodine rock matrix were in the order of 10^{-13} m^2/s and 10^{-12} m^2/s respectively and not affected significantly by pH. (English)

Migration of Cesium, Strontium and Cobalt in Water-Saturated Concretes

K. Idemitsu, H. Furuya, R. Tsutumi, S. Yonezawa,
Y. Inagaki and S. Sato

Scientific Basis for Nuclear Waste Management XIV,
p. 427-432. L. H. Johnson et al., eds., Material
Research Society (1991)

Diffusivities of Cs, Sr and Co were measured in several kinds of water-saturated concretes. The measured penetration profile of every tracer was composed of two parts. Those were a step slope near the surface and gradual slope in the deeper part. This profile was successfully explained by considering two diffusion paths in concrete. One diffusion path was possibly fissure with a width of a few microns and another was network of submicron pores. The volume of submicron pores was approximately 90% of the total free space volume in every concrete. The orders of magnitude of apparent diffusivies for all tracers were 10^{-12}-10^{-11} m^2/s through the fissue and 10^{-16}-10^{-15} m^2/s through the network of pores. The difference between the diffusivities of the two paths is thought to be caused by small geometrical factor of the network of submicron pores. (English)

Diffusion of Hydrogen and Deuterium in Zirconium under Cathodic Polarization

Tadahiko Mizuno

J. Japan Inst .,Metals, Vol. 55, No. 5, 553-557 (1991)

The diffusion behaviour of hydrogen and deuterium in Zr during cathodic discharge was studied by direct measurement of their concentration. These were estimated by a volumetric measurement of the chemical dissolution of the metal hydride layer and a d-d fusion method of deuteron bombardment to the metal layer including deuterium. The diffusion behaviour was analysed with a simple push model that the diffusing hydrogen or deuterium atom interact diffusion for hydrogen and deuterium in their hydride layer showed the same value of 49.0 kJ/mol and they were almost the asme as in other papers. But the diffusion coefficients of hydrogen (D_{DH}) and deuterium (D_{HD}) showed a big difference; the ratio of $D_{DH}/D_{HD}=14.4$ is extremely large compared with another value of nearly 3 obtained using a conventional diffusion model. The reason for the big difference is considered as follows. The diffusion process can be divided into several stages of the fundamental process. They are the discharge of the hydrogen ion from the solution to metal surface adsorption, the dissolution to metal from the surface, the diffusion through the hydride layer and the combination with the metal atom. The ratio of D_{DH}/D_{HD} for this model has a value of less than 4. But in the case of the push model in which the hydrogen atoms interacts with each other, the ratio becomes 11.3. (Japanese)

Tritium Evolution During Cathodic Polarization of Palladium Electrode in D_2O Solution

Tadahiko Mizuno, Tadashi Akimoto, Kazuhisa Azumi
and Norio Sato

J. Electrochemical Soc., Vol. 59, No. 9, 798-799 (1991)

Tritium was detected by conventional liquid scintillator method for a electrolyte during cathodic electrolysis of Pd rod in D_2O-LiOD system. Electrolysis was performed in a perfectly sealed cell made of stainless steel in which a Pt catalyst was fixed as a recombination of deuterium and oxygen gas released with the reaction into heavy water. Neutron evolutions during deuterium loading and release were measured as concerned with the D/Pd ratio and temperature. There is no clear relationship between the ratio and loading cycle and temperature. However, neutrons were detected when the D/Pd ratio was up to about 0.4. After three times deuterium loading, tritium concentration in the electrolyte was estimated; the concentration was increased 45% compared before electrolysis. The increase was 3×10^{11} atoms of ^3H after the reaction.

The ratio of the reaction rate of neutron and tritium production showed large discrepancy as 10^{-4} times. (Japanese)

Simultaneous Measurements of Acoustic Emission and Differential Thermal Analysis for Different $KClO_4$ Samples

Shiro Shimada, Yuji Katsuda, Ryusaburo Furuichi
and Michio Inagaki

Thermochimica Acta, **184,** 91 (1991)

Simultaneous measurements of acoustic emission (AE) and differential thermal analysis (DTA) were made for three types of $KClO_4$ samples (powders, dendrite crystals and one single crystal) using a home-made AE-DTA apparatus. Sensors of resonated frequency 140 KHz, 500 KHz, 1 MHz and 1.5 MHz were used. Irrespective of the type of sample, $KClO_4$ gives low and high temperature AE peaks at temperatures of 180–330°C and 560–640°C respectively. Scanning electron micrograph observation showed that the low temperature AE peak results from the break-up of large particles (crystals) and/or liquid release from their surface. The AE signals due to the transition of $KClO_4$ from orthorhombic to cubic form overlap with the low temperature peak and become more appreciable with increasing resonance frequency of the sensor. The high temperature AE peak consists of three peaks, *a*, *b* and *c*. The lower temperature part (560–590°C) of peak *a* is attrib-uted to a precursory event of the melting. Peaks *a* and *b*, which suggest a two-step decomposition, exhibit different frequency dependencies. Peak *c*, due to the solidification of molten KCl product, does not vary with the type of sample. In the case of a single crystal, an independent intense peak appears as the precursory event of the melting at 550–590°C. (English)

A Study on the Thermal Decomposition of $KClO_4$ by Acoustic Emission Thermal Analysis: Influences of Particle and Sample Size on Acoustic Emission Curve

Shiro Shimada, Yuji Katsuda and Ryusaburo Furuichi

Thermochimica Acta, **183,** 365 (1991)

In previous papers the authors described a new apparatus for the simultaneous measurement of acoustic emission (AE) and differential thermal analysis (DTA) and its successful application to the decomposition, dehydration and phase transition of several inorganic salts. In the case of $KClO_4$, it was shown that on the AE count-rate curve, one broad peak appears at 200–340°C and three sharp peaks appear at 560–660°C. Further experiments showed that the low temperature AE peak is greatly reduced by grinding the sample, while two of the high temperature peaks partially overlap as the sample mass decreases. This work reports the influence of the particle and sample sizes on the low and high temperature AE peaks associated with the phase transition and decomposition of $KClO_4$. (English)

Acoustic Emission Thermal Analysis

Ryusaburo Furuichi and Shiro Shimada

BUNSEKI (Anal. Chem. Soc, Japan.) (2), 94 (1991)

This review describes the principle and the assembly of devices for Acoustic Emission Thermal Analysis (AE). The applicability of AE was illustrated with thermal decomposition reactions of NaN_3, $NaClO_4$ and $KClO_4$, and with phase transition of KNO_3. (Japanese)

Piezoelecric Detection of Oxide Formation and Reduction on Platinum Electrode

Xiang Chung Jiang, Masahiro Seo and Norio Sato

J. Electrochem. Soc., **138,** 137-140 (1991)

Piezoelectric detection of change in surface stress, produced by a potential modulation, was applied to investigate oxide formation and reduction on platinum electrodes in perchloric acid solutions, in the presence and absence of chloride ions. In the solution without Cl^- ions, piezoelectric signals indicated that rerrangement or place exchange of surface atoms took place prior to monolayer formation of PtO and induced a sign reversal of the surface electric charge. Addition of Cl^- ions into the solution retarded the discharge reaction of adsorbed water molecules but promoted the rearrangement or place exchange of surface atoms. The PtO formation took place on a small fraction of surface sites via displacement or a substitution step of adsorbed Cl^- ions, and contributed to the sign-reversal of surface charge. (English)

X-Ray Photoelectron Spectroscopic Analysis of Surface Products on Pyrite by Bacterial Leaching

H. Konno, K. Sasaki, M. Tsunekawa, T. Takamori
and R. Furuichi

BUNSEKI KAGAKU, **40,** 609 (1991)

Bacterial leaching is often applied to recover useful metallic elements from low grade ores; an understanding of the leaching mechanism is necessary to improve the efficiency of this process. In the present work, surface analysis by XPS was carried out on pyrite (FeS_2) after leaching with *Thiobacillus ferrooxidans* for 1 to 11 d. The measured complex spectra were analyzed by the concept of differential charging effects; it was found that Fe(II, III), S, SO_4^{2-}, and probably SO_3^{2-}, are formed on the pyrite. The accumulation of K^+ ions was also found with more than 6 d of leaching. Although the observed elemental S is considered to be an intermediate product in the indirect leaching mechanism, the formation on pyrite particles during the bacterial leaching has not been directly observed. The assignment of the SO_3^{2-} peak is still conditional but, as a metabolic intermediate, the formation of SO_3^{2-} ions in the cell has been proposed by others. The time variations in the mole ratios of species of S or K *vs.* Fe in the surface products are helpful to understand the leaching mechanism. The accumulation of Fe(III), SO_4^{2-}, K^+ and OH^- ions on the surface with leaching suggests the formation of insoluble compounds, such as jarosite (chemical formula: $K[Fe_3(SO_4)_2(OH)_6]$). (Japanese)

In situ Fourier Transform Infrared Reflection Absorption Spectroscopic Studies of the Effects of Tin on the Electrochemical Oxidation of Carbon Monoxide on Polycrystalline Platinum

In Tae Bae, Takeshi Sasaki and Daniel A. Scherson

J. Electroanal. Chem., 297 (1991) 185-195

The modifications in the mode of bonding of CO on polycrystalline Pt in perchloric acid electrolytes induced by the presence of tin have been examined using in situ Fourier Transform Infrared Reflection Absorption Spectroscopy. It has been concluded, based on the results obtained, that tin adsorbs on a CO-saturated Pt surface displacing up to half of the oroginal CO, and brings about a sizable reduction in the overpotential for CO electroxidation. In addition, the integrated intensity of the CO peak normalized by the integrated intensity of the CO_2 peak obtained after full CO oxidation appears to be much higher than the corresponding value observed on a tin-free Pt surface. This effect is especially marked for moderate tin coverages at potentials negative to the onset of CO oxidation and has been tentatively associated with the presence of CO on special sites on the tin-free polycrystalline Pt surface for which the IR cross sections are very small. (English)

Cobalt (IV) Amine Complexes with Organic Ligands. XI. The Preparation and Properties of Tetraammine-(7-chloro-5-nitro- or 5,7-dinitro-8-quinolinolato)-Cobalt (IV) Complexes and the Corresponding Cobalt (III) Complexes

Yoshihisa Yamamoto, Eiko Toyota and Hidetaka Konno

Bull. Chem. Soc. Jpn., **64**, 1398 (1991)

Tetraammine-(7-chloro-5-nitro- or 5,7-dinitro-8-quinolinolato)-cobalt (IV) complexes and the corresponding cobalt (III) complexes have been isolated, and characterized by analytical, spectroscopic, magnetic, and XPS methods. The effective magnetic moments of cobalt (IV) complexes were ca. 1.6 BM, suggesting an unpaired spin. An unpaired spin on the complex is located over the π-orbitals of the 7-chloro-5-nitro- or 5,7-dinitro-8-quinolinolato ligand (abbreviation : chelated ligand) and on the cobalt atom from the results of the C 1s and Co 2p spectra by XPS. The Cl 2p binding energy of the chloride ion suggests that the valence electrons of the chloride ions may have some interaction with the π-orbitals of the chelated ligand. (English)