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ELECTROCHEMISTRY LABORATORY

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

Students

K. Araki, I. Sawamura, Tomonari Fujita, S. Ishiguro, T. Ikegami,
K. Fushimi, M. Aomi, K. Kasahara, Toshikatsu Fujita,
Y. Furukawa and K. Matsumura

Professor N. Sato retired Hokkaido University at the end of March, 1990 and Dr. M. Seo was promoted to new professor of the electrochemistry laboratory. 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 and anodic oxidation.

Piezoelectric Response to Surface Stress Change of Pd Electrode in sulfate solutions

The interfacial properties of palladium electrode in sulfate solutions of different pH values have been investigated from the piezoelectric response of surface stress change induced by a potential modulation. The piezoelectric signals indicated that the potential of zero charge is location in the potential region of hydrogen absorption into Pd. It was found that the sign-reversal of surface charge takes place at the potential of PdO monolayer formation which is similar to that of Pt.

Membrane Potential of Nickel Hydroxide Prepared on Platinum Net Electrode

Nickel hydroxide was cathodically deposited on platinum net electrode from 0.1 M $Ni(NO_3)_2$ solution. The membrane potential of the hydroxide was measured in NaCl solutions with different concentrations (10^{-4} M–1 M) to investigate the ion-selective properties. The nickel hydroxide as received was anion-selective. The anodic polarization of the hydroxide to form NiOOH, however, made change from anion-selective to cation-selective.

In-Situ Gravimetry of Anodic Deposition of Ferric Oxy-hydroxide Films by QCM

A quartz crystal microbalance (QCM) technique was applied to investigate anodic deposition process of ferric-hydroxide films on gold in three different kinds of electrolytes (perchlorate, phosphate and borate) containing ferrous ions. The apparent molecular weight of the deposited films was evaluated from comparison between the results obtained by in-situ gravimetry and coulometry. The apparent molecular weight of the deposited films thus evaluated strongly depended on the electrolytes, which was attributed to anodic oxidation of ferrous complex ion containing different electrolyte anions.

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 in a sulfuric acid solution has been investigated by comparing the film formation behavior on ADC-12 with that on Al-Si-Cu ternary alloys prepared by casting and rapid solidification. Low film formation efficiency on ADC-12 was due to high O_2 gas evolution rate, and a microstructure of the metal substrate produced by rapid solidification was responsible for the gas evolution.

Anodizing of Aluminum Covered with Thermal Oxide film

Thermally oxidized aluminum has been anodized in a neutral borate solution to examine the effect of the thermal oxide film on the structure and formation of anodic barrier oxide film. The anodic oxide film formed on heat-treated aluminum consisted of γ-alumina and showed a small value for film thickness/formation voltage, 0.75 nm/V.

Cathodic Polarization of Aluminum Covered with Anodic Barrier Oxide Film

Cathodic polarization behavior of aluminum electrode covered with anodic barrier oxide films has been examined by potential sweeping and potentiostatic polarization. The polarization curve obtained by potential sweep method did not depend on the thickness of the anodic oxide film. During potentiostatic polarization at -2.0 V to -3.0 V (vs. Ag/AgCl), small pits were generated and grew as current increased.

In-situ Measurement of the Passive Film by Tunneling Spectroscopy

Tunneling spectroscopy was developed as a "in-situ" technique for measurement of electrodes in electrolyte. In this technique a sharpened platinum tip was approached to the electrode surface where tunneling current flows. Then bias voltage applied between the tip and the electrode was scanned quickly, and a tunneling current vs. bias voltage curve was obtained. Tunneling current was also measured as a function of the electrode potential. For a passivated iron and a passivated titanium electrode tunneling current vs. bias voltage curve and tunneling current vs. electrode potential curve were understood as a change in the tunneling probability of electron through the space charge layer in the n-type semiconductive passive films on iron and titanium.

Diffusion Process of Hydrogen/Deuterium through Palladium

A resent topics in electrochemistry is the "Freischmann-Pons effect" (cold fusion). Concerning the phenomena a diffusion process of hydrogen and deuterium through Pd sheet was investigated by using FR (Frequency Response) Method. Hydrogen/deuterium was evolved on a side of Pd sheet by cathodic polarization at constant current and charged immediately into Pd. On another side of Pd sheet hydrogen/deuterium which had permeated through Pd sheet from the charging side was oxidized. In FR method charging current was a.c. modulated and compared with anodic current to evaluate the diffusion constant. Permeation efficiency of hidrogen/deuterium through Pd was also measured as a function of charging current density and solution pH. The efficiency of electrochemical charging of hydrogen/deuterium to Pd was larger in acidic solution than alkaline solution like as LiOH+H_2O/LiOD+D_2O.

Other Activities

Hokkaido University conferred on Prof. N. Sato the title of Professor Emeritus after his retirement. From April 1st, Prof. N. Sato became the Dean of Hokkaido Branch at the University of the Air which is located within the same campus of Hokkaido University. On June 1st., Dr. H. Takahashi moved from Analytical Chemistry Laboratory to this Laboratory as associate professor. Prof. M. Seo attended the 178th. Meeting of the Electrochemical Society which was held in Seattle, Washington, U.S.A. on October 14–19, 1990 and presented a paper entitled "Study on Corrosion of Copper Thin Film in Air Containing Pollutant Gas by a Quartz Crystal Microbalance".

The following scientists from over the sea visited this Laboratory in this year of 1990: Professors K. L. Tan and P. P. Ong from National University of Singapore, Singapore on March 30–April 3, Professor O. A. Petrii from Moscow State University, U.S.S.R. on April 18, Professor R. W. Staehle from University of Minnesota, U.S.A. on July 21–24, Dr. Matlosz from Ecole Polytechnique Federale de Lausanne, Switzerland on November 1, Professor S. Hofmann from Max-Planck-Institute fuer Metallforschung, Germany on December 27.

Oral Presentation

Monitoring of Corrosion of Copper Thin Films in Air Containing Small Amount of Pollutant Gas by Quartz Crystal Microbalance; I. Sawamura, M. Seo and N. Sato: The 16th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan., 1990

Surface Coating of Aluminum with MOCVD-Titanium Oxide and Pitting Corrosion Resistance; T. Sakamoto, M. Seo, S. Furuya and N. Sato: *ibid.*, Jan., 1990

Corrosion of Al in Boiling Neutral Phosphate Solutions; H. Takahashi, M. Yamaki and R. Furuichi: *ibid.* Jan., 1990

Anodizing of Rapidly Solidified Al-Si Alloys in Sulfuric Acid Solution; K. Watanabe, H. Takahashi and R. Furuichi: *ibid.* Jan., 1990

Effect of Phosphate Ion Concentration on the Reaction between Aluminum and Hot Water; H. Takahashi, M. Yamaki and R. Furuichi: The 81st Annual Meeting of Metal Finishing Soc, Jpn., March, 1990

QCM Measurement of Copper Thin Films in Air Containing Small Amoumt of Pollutant Gas; I. Sawamura, M. Seo and N. Sato: '90 Spring Meeting of the Jpn. Soc. Corros. Eng., May, 1990

Study on Anodic Oxidation of p-Si by Electroluminescence Measurement; M. Seo, K. Aotsuka, K. Fushimi and N. Sato: *ibid.*, May, 1990

Titanium Oxide Coating of Aluminum Surface by a MOCVD T. Sakamoto, M. Seo, N. Sato, F. Jitou, M. Mabae and S. Furuya: The 78th Spring Meeting of the Jpn. Light Metal Soc., May, 1990

Hydroxide Films on Aluminum Formed in Neutral Phosphate Solutions; H. Takahashi, M. Yamaki and R. Furuichi: The 177th meeting of Electrochem. Soc., May, 1990

Effect of Heat Treatment on the Formation of Barrier Anodic Oxide Film on Aluminum; C. Ikegami, H. Takahashi, R. Furuici and M. Seo The 1990 Summer Meeting of the Hokkaido Sections of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem., July, 1990

In-situ Measurement of Metal Surfaces by Using Piezoelectric Properties; M. Seo: The 158th Tech. Meeting of Corr. Eng. Div., The Soc. of Mater. Sci. Jpn., Sept., 1990

Study on Corrosion of Copper Thin Film in Air Containing Pollutant Gas by a Quartz Crystal Microbalance; M. Seo, I. Sawamura and N. Sato; The 178th Meeting of The Electrochemical Soc., Seattle, Washington, U.S.A., Oct., 1990

Anodizing of Aluminum Covered with Thermal Oxide in a Neutral

Borate Solution ; C. Ikegami, H. Takahashi, R. Furuichi and M. Seo : The 82nd Annual Meeting of Metal Finishing Soc. Jpn., Oct., 1990

NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. H. Ohashi, Assoc. Prof. Dr. S. Sato, Dr. T. Mizuno,
Mr K. Hirohara and Mrs. N. Ochiai

Students

Febrianto, H. Kobayashi, Y. Sugita, M. Yoneyama, C. Oda,
Y. Sekine, S. Tasiro, K. Yamazaki and M. Yoshida

The laboratory is concerned with investigations on corrosion of metallic materials used in nuclear industry, cha-racterization of iron rust components, development and improvement of hydrogen reservoir alloys, elucidation 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 measurement.

(2) The dissolution rate of magnetite were measured in aqueous solutions of 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 change of the hydrogen storage materials by acoustic emission, and by absorption and desorption of hydrogen were investigated. Change in lattice parameters and Mössbauer spectra were determined as a function of annealing and absorption and desorption cycle of hydrogen.

(4) Pitting corrosion of iron was investigated in buffered solutions by in-site spectrum analysis of fluctuation of corrosion current. Growth of pits was detected by variation of spectrum of change in the current in pits.

(5) Migration behavior of noble metal fission products in uranium dioxide was investigated by characterizing uranium dioxide pellets containing Pd and Mo by measurements of O/U ratio and density,

ceramographic observations, and EPMA.

(6) The diffusion of cesium., iron, cobalt and chromium ions compacted bentonine was investigated in connection with nuclide migration in the engineered barrier and the rate of corrosion of canister in the geological disposal of radioactive wastes.

(7) The redox state of iron, ions in simulated waste glass was investigated, and the evidence of a complex precipitated phase was found.

(8) Algorithm and program were developed for analysis of Mössbauer spectra by the programming language C. The FFT and Gauss Neuton method were applied in the algorithm, and it was found that the computing rate is less that about fifteenth, compared with BASIC.

Oral Presentation

Disposal and Its Safety Assessment of High Level Radioactive Wastes; H. Ohashi: The International Meeting on the Education of Peaceful Uses of Atomic Energy, Aug., 1990, Misawa

Neutron evolution from Pd electrode by cathodic polarization under high pressure and high temperature; T. Mizuno, T. Akimoto and K. Azumi: Minisimposium of Cold Fusion, Sep., 1990.

Neutron evolution from Pd electrode caused by cathodic polarization in an auto cleave; T. Mizuno, T. Akimoto and K. Azumi: The FallMeeting of Electrochemical Society, Sep., 1990.

Overview on Research and Development of Radioactive Waste Disposal in European Countries; S. Sato: Lecture at Hokkaido Electric Power Co., Inc. Sep., 1990.

Migration of Cesium, Strontium and Cobalt in Water-Saturated Concretes; K. Idemitsu, H. Furuya, R. Tsutsumi, S. Yonezawa, Y. Inagaki and S. Sato: Materials Research Society Fall Meeting, Nov., 1990.

Helium Behavior in actinide-doped radioactive Waste glass; K. Morikawa, S. Sato, H. Furuya, S. Matsumoto and S. Tashiro: Annual meeting of Hokkaido-branch of Atomic Energy Society of Japan, Dec., 1990.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Rrof. Dr. H. Tamura,
Dr. H. Konno and Miss Y. Hori

Students

S. Tamura, M. Tokita, K. Watanabe, A. Furusaki, M. Kudo,
K. Ishizeki, M. Watanabe, S. Matsugi and H. Ito

This year, Prof. Furuichi was serving as the chairman of the Hokkaido Section of the Surface Finishing Society of Japan (SFSJ). Prof. Furuichi and Dr. Konno were awarded a prize for their paper "Electrochemical Formation of Zr(IV)-Cr(III) or Ti(IV)-Cr(III) Composite Oxide Films on Stainless Steel" by SFSJ in March. Dr. Konno participated in the Electrochemical Society Meeting, Montreal, in May. In June Dr. Takahashi moved to the Applied Electrochemistry Laboratory, Faculty of Engineering, Hokkaido University, as an associate professor.

The research programs in our laboratory are:

(1) *Characterization of iron oxides and oxyhydroxides.*

Different FeOOH powders were prepared from aqueous solutions with different aging periods in the solution and calcinated at different temperatures. Surface and bulk characterization of the formed oxide powders were carried out by XRD, TG-DTA, surface area measurement (BET), determination of the surface hydroxyl groups, and acid-base titration of oxide suspensions.

(2) *Incorporation of impurity metal ions into electrolytic manganese dioxide.*

The amounts of impurity metal ions incorporated into MnO_2 during electrolytic preparation were measured as a function of metal ion concentrations and current densities. The incorporation increased with the concentration. With increasing current densities, Fe^{3+} decreased, but Cu^{2+}, Co^{2+}, and Ni^{2+} increased. The anode potential and the BET specific surface area of MnO_2 increased with the current density. The incorporation was considered to occur through the adsorption of ions on MnO_2 particle surfaces, and the effect of current density was explained in terms of increasing surface area (promotion) and increasing anode potential (suppression).

(3) *Adsorption of Li^+ and other alkali metal ions on manganese dioxide.*

The amount of exchanged alkali metal ions with surface hydroxyl protons was measured as a function of pH. It increased in the order · $Cs^+ < K^+ < Na^+ < Li^+$ at higher pH values. The behavior was analysed and it was found that the affinity of Li^+ for MnO_2 is the lowest, but the suppression of the exchange by adsorbed Li^+ is the smallest, and the amount of Li^+ adsorbed becomes the largest at higher coverages. The results obtained will provide a basis for understanding a) the function of Mn oxide as Li^+ collectors from sea water and b) the interaction between Li^+ and MnO_2 in dry cells.

(4) *Adsorption of divalent metal ions on metal oxides.*

The amount of Mn(II) ions adsorbed by MnO_2 was measured, and it was far larger than Co^{2+}, Ni^{2+}, and Zn^{2+}. An XPS analysis suggested that Mn(II) ions were oxidized by MnO_2 to Mn(III), which may be repsonsible for the higher affinity of Mn(II) for MnO_2. The adsorption behavior of Co^{2+}, Ni^{2+}, and Cu^{2+} for systems where two of these ions are present, a) $Co^{2+}+Cu^{2+}$ and b) $Co^{2+}+Ni^{2+}$, was studied. At high concentrations, the amount of adsorbed ions are lower than that with only one type of ions, indicating a suppression by the other ions adsorbed.

The adsorption of Co^{2+} on Al_2O_3 was measured, and the abilities of MnO_2, Fe_3O_4, and Al_2O_3 for Co^{2+} adsorption were compared.

(5) *Polyfunctionality of resin carboxyl groups for alkali metal ions.*

Polyfunctionality of resin carboxyl groups was further investigated by examining the exchange behavior of alkali metal ions with an weak-acid type ion-exchange resin (IRC–84). The behavior was analysed with the model developed here, and it was concluded that two exchange reactions take place in the resin: 1) with hydrated ions in loosely cross-linked resin portion and 2) with dehydrated ions in tightly cross-linked portion.

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

A method to form perovskite structure lanthanum chromium oxide ($LaCrO_3$ and $La_{1-x}M_xCrO_3$, M=Ca or Sr) films on metals was developed. The method consists of (i) the formation of precursor films, $(LaOH)_{1-x}M_xCrO_4\ nH_2O$, on metals by cathodic deposion from chromate solutions containing La and Ca or Sr ions, and (ii) the pyrolysis of the precursor films. This year, the method was developed to form films having the maximum x value of 0.2 with Sr, and surveying the pyrolysis condition under nitrogen atmosphere was carried out. Further, by replacing the above second step by laser irradiation, $LaCrO_3$ particle dipersed alloy layer was formed on stainless steels. The method was found to provide excellent oxidation resistance to ordinary stainless steels such as Type 304 and 430 at above 1000°C.

(7) *Synthesis of substituted lanthanum chromium oxides having perovskite structure.*

A method to synthesize A-site substituted lanthanum chromium oxide, $La_{1-x}M_xCrO_3$ [M=Ca(II) or Sr(II)], and B-site substituted lanthanum chromium oxide, $LaCr_{1-x}M_xO_{3+d}$ [M=Mn(III)] powders was developed using La(III), Cr(VI), Ca(II), Sr(II), and Mn(II) compounds as starting materials. The method enabled the perovskite structure oxides to be formed with lower energy consumption than conventional methods. The formation mechanism was investigated by TG–DTA, XRD, IR, EPR, and chemical analysis.

(8) *Composition of oxide films formed during an initial period of high temperature oxidation.*

The project is continuing and a design for a new oxidation apparatus has started to control oxidation time (30 to 90 s), atmosphere (both oxidizing and reducing), and temperature (max. 1400°C) to extend the project to commercial stainless steels. Further, accurate surface analysis procedure by XPS was establshed.

(9) *Atmospheric Corrosion of SENDUST*

The SENDUST is Fe-Si-Al magnetic alloy which show very high initial permeability around 85 Fe-10 Si-5 Al. It is known that corrosion resistance of this alloy is improved by doping with high valence metal such as Nb, Ti, V, and Zr. At the start, corrosion behavior of standard SENDUST, 0.3 mass% Nb doped SENDUST, and 99.99% pure iron was investigated in humid air at 80°C. It was found that the effect of Nb is different for different relative humidities. Further investigation is continuing.

Oral Presentation

High Temperature Oxidation Behavior of the Stainless Steels Coated with Lanthanum Chromium Composite Oxide: S. Kitazaki, H. Konno and R. Furuichi: The 16th Meeting of the Hokkaido Sec. of Electrochem. Soc. Jpn, Jan., 1990.

Composition of the Film Formed on Iron Chromium Alloys by Very Short Period Oxidation at an Elevated Temperature; H. Konno and R. Furuichi: *ibid.*

Description and Prediction of Ion-Exchange Equilibria; H. Tamura, T. Oda and R. Furuichi: *ibid.*

Synthesis of the Perovskite Structure Lanthanum Chromium Composite Oxide from La(III)-Cr(VI) Solutions; A. Furusaki, H. Konno and R. Furuichi: The 1990 Winter Meeting of the Hokkaido Secs. of Jpn Soc. Anal. Chem. and Chem. Soc. Jpn., Feb, 1990.

Formation of Substituted Rare Earth Chromium Composite Oxide Films on Ni by Electrodeposition; M. Tokita, H. Konno and R. Furuichi: *ibid.*

Preparation of Supported High Activity Molybudenum Sulfide Catalyst; T. Katsuma, M. Sugioka, T. Kanazuka and H. Konno:

ibid.

Solid/Solution Distribution of Co^{2+} Ion with MnO_2; S. Tamura, H. Tamura and R. Furuichi: *ibid.*

Formation of the Rare Earth Composite Oxide Particle Dispersed Alloy Layer by Laser Mixing; H. Konno, S. Kitazaki and R. Furuichi: The 80th Meeting of Surf. Finish. Soc. Jpn, Mar., 1990.

Electrochemical Formation of Zr(IV)-Cr(III) or Ti(IV)-Cr(III) Composite Oxide Films on Stainless Steels; H. Konno and R. Furuichi: *ibid.* (A lecture in honor of receiving the society's Prize)

Characterization of the Acid-Base and Ion-Exchange Behavior at Metal Oxide/Aqueous Solution Interfaces; H. Tamura: KDK Seminar, March 1990.

A New Proposal for the Selectivity Coefficient of Ion Exchange and Characterization of Ion-Exchange Behavior with the Proposed Model; H. Tamura, T. Oda and R. Furuichi: The 59th Spring Meeting of Chem. Soc. Jpn., April 1990.

Electrochemical Formation of Perovskite Type Lanthanum Chromium Oxide Films and Applications to Alloys; H. Konno: Seminar at NRC Canada (Ottawa), May, 1990.

Electrochemical Formation of Perovskite Structure Lanthanum Chromium Composite Oxide Films; H. Konno, M. Tokita, S. Kitazaki and R. Furuichi: The Electrochemical Society 177th Meeting (Montreal), May, 1990.

Composition of the Initial Oxide Film Formed on Iron Chromium Alloys by High Temperature Oxidation in a H_2O/O_2 Atmosphere; H. Konno and R. Furuichi: Fushoku-Boshoku '90, May, 1990.

Synthesis of the Perovskite Structure $La(Cr_{1-x}Mn_x)O_3$ by pyrolisis; A. Furusaki, H. Konno and R. Furuichi: The 1990 Summer Meeting of Hokkaido Secs. of Chem. Soc. Jpn. and Jpn Soc. Anal. Chem. July, 1990.

Adsorption of Mn^{2+} Ions on MnO_2 and the Oxidation State of Adsorbed Mn Ions; S. Tamura, H. Tamura and R. Furuichi:

ibid.

High Temperature Oxidation Behavior of the $LaCrO_3$ Particle Dispersed Alloy Layer Formed by Laster Irradiation; H. Konno and R. Furuichi: The 37th Ann. Symp. on Corrs. and Protection, Aug., 1990.

Exchange of Na^+ Ions with Resin Carboxylic Protons-Two Kinds of Exchange Sites with Different Reactivities and Equilibrium Conditions—; H. Tamura, T. Oda and R. Furuichi: 6th Jpn. Assoc. Ion Exchange, Sept. 1990.

Formation of Substituted Lanthanum Chromium Composite Oxide Films by Electrodeposition; M. Tokita, H. Konno and R. Furuichi: The 81st Meeting of Surf. Finish. Soc. Jpn., Oct. 1990.

Structure and Composition of the $LaCrO_3$ Particle Dispersed Alloy Layer Formed by Laser Fusing; H. Konno and R. Furuichi: *ibid.*

Codeposition of Impurity Metal Ions into Electrolytic Manganese Dioxide; H. Tamura, K. Ishizeki R. Furuichi and M. Nagayama: IBA San Paulo Meeting, Oct. 1990.

Formation of $LaCrO_3$ Particle Dispersed Alloy Layer as a Means for Improving Oxidation Resistance; H. Konno and R. Furuichi: Intl. Symp. Solid State Chemistry of Advanced Materials, Dec., 1990.

ELECTROMETALLURGY LABORATORY

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

Students

K. Miura, T. Kumagai, T. Mitsueda, Y. Shibata, S. Kawamori,
H. Tanaka, M. Maeda, Marusudi Wibowo, M. Tomioka,
M. Noguchi, M. Huto, T. Huruna, T. Matsutani
and T. Moriyasu

Professor Ishikawa participated in the 177th ECS Meeting held in Montreal in May and also attended the Third China-Japan Bilateral Conference on Molten Salt Chemistry and Technology in September 1990.

Associate Professor Narita attended the 29th CIM Meeting held in Hamilton, Canada, August 1990, and also he joined to the First Japan-China Symposium on Joinings of Dissimilar Materials held in Tokyo, November, 1990 and International Symposium on High-Temperature Corrosion held in Tokyo, December, 1990.

Dr. Notoya participated in the 11th International Corrosion Congress in Florence, Italy, 2nd-5th, April.

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.

[illegible]

(2) In order to save much energy in producing pure aluminum from aluminum scraps, an electrochemical cycle system in molten salts was developed and the characteristics of the aluminum-chlorine fuel cell as ~~an element~~ a process of the ~~cycle~~ system are under study.

(3) A novel galvanic cell for the reduction of the oxygen concentration in ~~fresh~~water in pipe lines was developed and its performance

tap water

is under investigation.

(4) Sulfidation and reduction behavior of the preformed oxide scales on an Fe-25Cr-5Al and Fe-25Cr-5Al-Y alloys were investigated at 973 K in the H_2S-H_2 atmospheres.

(5) Ceramics-metal joinings: bonding systems investigated are as follows. Si_3N_4 and Fe-25Cr alloy with Ni-Cu-Ti filler, Al_2O_3 and Ni with Ag-Cu-Ti filler, and ZrO_2 and Cr with Ag-Cu-Ti filler.

(6) Tarnishing and inhibition mechanisms of copper and copper alloys were studied with some corrosion inhibitors by using electrochemical techniques and surface analysis. Preventive measures for localized corrosion in copper tubes have been investigating.

(7) 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 methods.

(8) Investigation into the in-situ spectroelectrochemical phenomena on adsorbed benzothiols on the surface of gold continues by using Fourier transform infrared reflection absorption spectroscopy.

Oral Presentation

Measurement of Thermal Residual Stress of Ceramics-Metal Joints by Scanning Acoustic Microscopy; T. Narita, K. Miura, T. Ishikawa and I. Ishikawa: The 22nd NDE Symposium, Jan., 1990.

On the Simulation Test of Ant Nest Corrosion in Copper Tubes; T. Notoya: Corrosion Commitee Workshop of Japan Copper Development Association, Jan., 1990.

Measurement of Conductivity and Decomposition Voltage of Chloride Melts Containing $MgCl_2$; N. Yokoyama, S. Konda, T. Narita and T. Ishikawa: The 16th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1990.

Characterization of $Al-Cl_2$ Fuel Cell in Molten Salt System; A. Ando, S. Konda, T. Narita and T. Ishikawa: *ibid.*, Jan., 1990.

The Effect of Tin on the Oxidation of Carbon Monoxide on Polycrystalline Platinum Electrode —in situ Observation with FTIR; T. Sasaki, I. T. Bae and D. A. Scherson: *ibid.*, Jan., 1990.

In situ Observation with FTIR of 2,5-Dihydroxythiophenol Adsorbed on Polycrystalline Gold Electrodes; T. Sasaki, I. T. Bae and D.A. Scherson: *ibid.*, Jan., 1990.

Corrosion Characteristics and Electrochemical Behavior of Brass in Cupric Chloride Solution; S. Hori, S. Konda, T. Narita and T. Ishikawa: The 25th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1990.

Effect of Benzotriazole and Phenyl-amino-triazine-dithiol on Corrosion Inhibition for Copper in Low Conductivity Water; T. Notoya, T. Ishikawa, Guo-ding Zhou and Yigi Feng: The 1990 Spring Meeting of Hokkaido Section of Japan Chemical Society, Feb., 1990.

Characterization of Aluminum-Chlorine Fuel Cell in Chloride Melts; M. Maeda, S. Ando, S. Konda, T. Narita and T. Ishikawa: The 57th Annual Meeting of Electrochem. Soc. Japan, Apr., 1990.

In situ Observation by IRRAS of Organic Materials Irreversibly Adsorbed on Electrode Surfaces; T. Sasaki, I. T. Bae and D. A. Scherson: *ibid.*, Apr. 1990.

Effect of Tin on Adsorbed States of Carbon Monoxide on Platinum Electrode Surfaces; T. Sasaki, T. Ishikawa, I. T. Bae and D. A. Scherson: *ibid.*, Apr., 1990.

Inhibition of Bata-phase Brass Dezincification by Organic Inhibitors; T. Notoya and T. Ishikawa: The 11th International Corrosion Congress, Apr., 1990.

High-Temperature Oxidation Behavior of Silicon-nitride Ceramics Joined to Metals; K. Miura, T. Narita and T. Ishikawa: The 106th Annual Meeting of JIM, Apr., 1990.

Electrowinning of Liquid Magnesium by Using a Stacked-Type Bipolar Electrode Cell; T. Ishikawa, T. Narita and S. Konda: The 177th Meeting of ECS, Montreal, May, 1990.

Influence of Corrosives on the Morphology of Localized Corrosion in Copper Tubes; T. Notoya and T. Ishikawa: Corrosion and Corrosion Prevention '90, May, 1990.

Effect of Benzotriazole and Related Organic Inhibitors on Corrosion Inhibition of Copper; T. Notoya and T. Ishikawa: The 10th Meeting of Japan Rust Prevention Assosiation, June 1990.

Simultaneous Measurement of Stress and Displacement of the Ceramic-Metal Joints by SAM; T. Narita, T. Ishikawa, T. Yoshida, T. Mitsueda and K. Miura: The Spring Meeting of Hokkaido Section of JIM, June 1990.

Formation of Al_3Ti from Liquid Al in Chloride Melts Containing Titanium Chloride; T. Kumagai, S. Konda, T. Narita and T. Ishikawa: *ibid.*, June, 1990.

On the Reproduction of Scrap Aluminum; T. Ishikawa: The Hokkaido Section Meeting of Japan Institute of Light Metals, June, 1990.

High-Temperature Sulfidation of Iron-based Alloys; T. Narita: Int. Sympo. on HIGH-TEMPERATURE OXIDATION AND SULFIDATION PROCESSES, Aug., 1990.

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Study on Corrosion of Copper Thin Film in Air Containing Pollutant Gas by a Quartz Crystal Microbalance

Masahiro Seo, Ichirou Sawamura and Norio Sato

Proc. of 1st Int. Symp. on Corr. Elect. Mater. & Devices,
Electrochem. Soc., **91-2,** 165-175 (1990)

A quartz crystal microbalance (QCM) technique was applied to investigate the corrosion kinetics of copper thin films at 303 K in air or nitrogen gas at different relative humidities containing small amount (20 ppm) of SO_2, H_2S or NO_2. The corrosion increased with increasing relative humidity and was promoted by oxygen in air. The corrosion kinetics and corrosion products were different depending on the species of pollutant gas. The relative humidity dependence of parabolic corrosion rate constant was explained in terms of the nonstoichiometry of corrosion products or their porous structures with easy diffusion paths. (English)

Measurement of a Trace Amount of Corrosion by QCM and SAW Techniques

Masahiro Seo, Yuuihi Ishikawa and Takashi Honda

Boshoku Gijutsu, **39**, 597–708 (1990)

Quartz crystal microbalance (QCM) and surafce acoustic wave (SAW) techniques, which are capable of detecting a trace amount of weight changes in the magnitude of 10^{-9} g•cm^{-2} from the changes of resonant frequency, are useful for monitoring a trace of corrosion of metal thin films. This article dealt with application of QCM and SAW to atmospheric corrosion and aqueous corrosion of metal thin films. Adsorption of water molecules, corrosion kinetics and corrosion mechanism of metal thin films were discussed on the basis of typical results obtained by QCM and SAW. Furthermore, it was shown that stress was one of predominant factors influencing the resonant frequency of QCM in the case of absorption of hydrogen or deuterium atoms into Pd thin films. (Japanese)

Measurement of Minute Corrosion of Copper Thin Film by a Quartz Crystal Microbalance

Masahiro Seo, Ichirou Sawamura, Lars Grasjo,
Yasuhiro Haga and Norio Sato

J. Soc. Master. Sci. Japan. **39**, 357–361 (1990)

A quartz crystal microbalance (QCM) technique can detect sensitively a small weight change during minute corrosion of metal thin film from the measurement of change in resonance frequency of quartz crystal. The QCM technique has been applied to monitor the minute corrosion of copper thin films in air or nitrogen gas with different relative humidities containing H_2S of 20 ppm at 30 °C.

The weight gain due to sulfide formation as corrosion products on the copper thin film obeyed a linear rate law at the initial stage and subsequently obeyed a parabolic rate law. The linear and parabolic rate constants obtained from the time-variation of weight gain were influenced by the relative humidity and oxygen in air. The corrosion mechanism was discussed from the view-point of electrochemistry.

Furthermore, the QCM technique has been applied to investigate the anodic oxidation process of copper thin film in pH 8.4 borate solution. The real electric current, I_{real} measured during anodic oxidation at a constant potential in the passive region was compared with the apparent current, I_{app} calculated from the frequency change in QCM. It was shown that the dissolution rate of Cu^{2+} ions through the passive film into solution and the uptake rate of oxygen in the film could be separately evaluated from the comparison between I_{real} and I_{app} at the high anodic potential where the dissolution of Cu^{+} ions was negligibly small.

These results have revealed that the QCM technique is one of the most powerful tools for the study on minute corrosion of metal thin film. (Japanese)

Ant Nest Corrosion in Copper Tubes

Takenori Notoya

Boshoku Gijutsu **39,** 315–320 (1990)

Uniform oxidation is the most common type of corrosion of copper tubes in heat-exchanging refrigerating and air-conditioning units. Recently an unusual type of corrosion, "ant nest corrosion", has been reported in such copper tubes at the final leakage test before shipment or a short time after installation. The corrosion is characterized by complicated microscopic caverns containing porous copper oxide connected by tunnels. The microcaverns have voids and cracks, and the surfaces of the copper tubes are tarnished dark-brown or red-brown without bulky corrosion products and show no obvious defects indicating the leaks. Sixty four cases of such premature failures of copper tubes discovered during the 11 years from 1978 to 1988 are listed in Table 1, including date of detection, application of copper tube, time to failure, wall thickness, location of attack, surface color and possible corrosives. Nomenclature for the localized corrosion and classification of different types of the ant nest corrosion with its size are also described. Nine typical structures of the ant nest corrosion are presented in the copper tubes for both air-conditioning units and simulation tests. (Japanese)

Ant Nest Corrosion in Copper Tubing

T. Notoya

Corrosion Engineering **39,** 353-362 (1990)

Uniform oxidatition is the most common type of corrosion in copper tubing in heat-exchanging refrigeration and air-conditioning units. Recently, an unusual type of corrosion, named ant nest corrosion, has been reported in such copper tubing at the time of the final leakage test before shipment, or a short time after installation. This corrosion is characterized by complicated microscopic caverns, containing porous copper oxide, connected by tunnels. The microcaverns have voids and cracks, and the surfaces of the copper tubes are tarn-shed to a dark-brown on reddish-brown color without bulky corrosion products, and show no obvious defects indicating leaks. Sixty-four cases of such premature failure of copper tubing that were discovered during the 11 years from 1978 to 1988 are listed in Table 1, including their date of detection, application of the copper tube involved, time to failure, wall thickness, location of corrosion, surface color, and possible corrosives. The nomenclature of this corrosion and the classification of different types of ant nest corrosion by size are also described. Nine typical structure of ant nest corrosion for copper tubes used both in air-conditioning units and in simulation tests are presented. (English)

Ant Nest Corrosion in Copper Tubes and its Classification

T. Notoya and T. Hamamoto

J. Japan Copper and Brass Research Association
Vol. 29 p. 109 (1990)

An unusual type of corrosion, "ant nest corrosion", has been reported in copper tubes in heat-exchanging, refrigerating and air-conditioning units at the final leakage test before shipment or a short time after installation. The corrosion is characterized by complicated microscopic caverns containing porous copper oxide connected by tunnels. The micro-caverns have voids and creacks, and the surfaces of the copper tubes are tarnished dark-brown or red-brown without bulky corrosion products and show no obvious detects indicating the leaks. Sixty four cases of such premature failures of copper tubes discovered during the 11 years from 1978 to 1988 are listed in Table 1, including date of detection, application incopper tube, time to failure, wall thickness, location of attack, surface color and possible corrosives. A new nomenclature and classification for the localized corrosion is presented. The ant nest corrosion observed in the cross section of the copper tubes can be classified by the following terms; (i) general corrosion type-G or pitting corrosion type-P, (ii) single pit-S or numerous pits-N, (iii) open type-0 or closed type-c, (iv) round shape-R or long shape-L, (v) width of pit mouth 1 in mm, (vi) maximum pit depth-D in mm, and (vii) D divided by wall thickness T in %, Nine typical structures of the ant nest corrosion in the copper tubes used for commercial air-conditioning units and simulation tests are shown and classified by the nomenclature. (Japanese)

Inhibition of Beta Phase Brass Dezincification by Organic Inhibitors

T. Notoya and T. Ishikawa

Proceedings of the 11th International Corrosion
Congress Vol. 3 p. 3. 39 (1990)

Preferential dezincification of β phase in binary phase brass is still a practical problem, although dezincification resistance has been improved by small additions of alloying elements and/or heat treatment to reduce the amount of β phase and disperse it in the matrix. A chemical approach to inhibit dezincification of a β single phase brass by the addition of organic inhibitors to corrosive environments was investigated. Four organic chemicals were evaluated under potentiostatic accelerated conditions by analysis of dissolved metals in a neutral solution of 0.5 M NaCl and 5 mM $NaHCO_3$ at 30°C and determination of dezincification layer thickness. The inhibitors were 1, 2, 3-benzotriazole (BTA), tolyltriazole (TTA), 1-(N-phenyl-6-amino)-1, 2, 5-triazine-2, 4-dithiol monosodium salt (PTD), and 1-(2, 3-dihydroxy propyl)-benzotriazole (BTA-GL). The PTD proved to be most effective followed by BTA, TTA, and BTA-GL. A combination of PTD and one of the other three showed a synergestic effect in inhibiting dezincification in the β phase brass. (English)

The Effect of Benzotriazole and Phenyl-amino-triazine-dithiol on Corrosion Inhibition of Copper in Low-conductivity Water

Zhou Guo-ding, Feng Yiqi and Takenori Notoya

Corrosion Engineering **39**, 411–417 (1990)

Impedance measurements of copper electrodes in a low-conductivity water (less than 10 μS/cm) with the addition of either benzotriazole (BTA) or phenyl-amino-triazine-dithiol (PTD) were performed. BTA inhibits copper corrosion better than PTD. Corrosion inhibition with PTD occurs only concentrations above 10 ppm. A combination of BTA and PTD proved more effective than either used alone. The optimum ratio is 3 ppm BTA+2 ppm PTD with the total amount of inhibitor 5 ppm. (English)

Anodizing of Al-Si Casting in a Sulfuric Acid Solution

H. Takahashi, K. Watanabe, S. Hashimoto and R. Furuichi

J. Metal Finishing Soc. Jpn., **41,** 423 (1990)

Al-Si casting alloys with Si contents (C_{si}) of 0-17 wt% and ADC12 die casting alloy were anodized in 10% H_2SO_4 at 20°C under a constant current density (i_a) to examine the anodizing characteristics and film properties of these alloys. The anode potential (E_a) and dissolution current of Al^{3+} (i_d) during anodizing, the average film thickness ($\bar{\delta}$) and the diffuse reflectance of films were examined as functions of the abrasion thickness (X) of specimens, anodizing time (t_a) and i_a.

The steady value of E_a, $E_a{}^*$, for the casting alloys was found to increase with C_{si} at $X=100\,\mu m$, and showed a maximum at $C_{si}=10$ wt% and $X=100\,\mu m$. The value of $E_a{}^*$ for ADC12 increased steeply with i_a, and was much larger than that for the casting alloys. Dissolution current efficiency, i_d/i_a, decreased with i_a, and C_{si}, independent of X, for both casting alloy and ADC12 specimens.

Oxide films formed after anodizing for 40 min showed thickness differences on both types of specimen, and the dispersion in the film thickness increased with C_{si} and i_a. The value of $\bar{\delta}$ for the casting alloys decreased appreciably with increasing C_{si}, independent of X, at current densities of less than 100 A/m^2, but increased with increasing X at 200 A/m^2. The value of $\bar{\delta}$ for ADC 12 was considerably smaller than that for the casting alloys, suggesting higher rates of side reaction such as oxygen evolution.

The diffuse reflectance spectra showed that the reflectance of films decreased with increasing C_{si}, and with decreasing X.
(Japanese)

Change of the Anodic Oxide Films of Tungsten during the Electrochromic Reaction

Toshiaki Ohtsuka, Noboru Goto and Norio Sato

J. Electroanal. Chem., **287**, 249 (1990)

A thin oxide film has been formed anodically on a tungsten electrode at a potential of 1.0 V (vs. RHE) in 0.1 mol dm^{-3} sulphuric and perchloric acid solutions. The composition and electrochromic behaviour of the film have been examined by in-situ ellipsometry and Raman spectroscopy. The anodic oxide film has a low refractive index of 1.64 and its in-situ Raman spectrum corresponds to that of a highly hydrated W(VI) oxyhydroxide containing a terminal W=O bond. The electrochromic colouring of the film takes place at a potential lower than 0.50 V and the light absorption increases with decreasing potential, where it is directly proportional to the amount of cathodic charge passed during the colouring process. The electrochromic reaction may be initiated by both electron transfer from the metal substrate and proton transfer from the aqueous acidic solution to the oxide. Electrons and protons may be trapped respectively, by tungsten ions and by the terminal oxygens of W=O sites, and the relatively slow change of the Raman signal for the oxide transformation indicates that a relaxation process exists for the formation of W-OH from the W=O site and the proton transferred. (English)

Formation of Hydroxide Films on Aluminum in Neutral Phosphate Solutions at High Temperature

H. Takahashi, M. Yamaki, R. Furuichi and M. Seo

J. Mineral. Soc. Jpn., **19,** 387 (1990)

Aluminum foil specimens were immersed in neutral phosphate solutions with $C_{an}=10^{-4}\sim10^{-1}$ M and doubly distilled water (DDW) for 60 min at 99.5°C, and the formation behavior of hydroxide films on the surface was examined by gravimetry, chemical analysis, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and impedance measurements.

In DDW, two-layer hydroxide films were observed with film formation efficiency, η, of 1.0, and in phosphate solutions, thin single-layer hydroxide films were observed with $\eta=0.7\sim0.9$. At $C_{an}=10^{-2}$ kmol/m^3, the film thickness showed a minimum and η a maximum. The XPS results showed that phosphates are incorporated in the outer part of the films formed in phosphate solutions, and that the phosphate incorporation increases with C_{an}. For all the films impedance measurements suggested the existence of an oxide layer with ca. 2.5 mm thickness at the interface between the hydroxide film and the metal substrate.

The role of phosphate ions in the formation of hydroxide films is discussed in terms of dissolution and stabilization of the film with aluminum-phosphate complexes. (Japanese)

The Role of Anions in the Formation of Hydroxide Films on Aluminum in Hot Aqueous Solutions

H. Takahashi, M. Yamaki and R. Furuichi

Corros. Sci., **31,** 243 (1990)

The formation characteristics of hydroxide films on aluminum were studied at 99.5°C in neutral solutions of citrate, silicate, and phosphate (10^{-4}–10^{-2} M) as well as in doubly distilled water (DDW), by gravimetry, chemical analysis, TEM, and XPS.

In silicate and phosphate solutions both the oxidation of aluminum and formation of hydroxide films are retarded with increasing anion concentration, and in citrate solutions the oxidation rate increases but the film formation rate decreases. TEM showed that all the films formed in the test solutions consist of one layer except with DDW and 10^{-4} M silicate solution, and the thickness decreased with increasing anion concentration. The film formed in DDW and 10^{-4} M silicate solution had a two-layered structure. According to XPS, appreciable amounts of silicate or phosphate were incorporated in the film formed in each solution.

The role of the anions on hydration of aluminum is discussed in terms of the stability and dissolution of surface films. (English)

Two-layer Structure and Ion Selectivity of Iron Passive Film Affecting Pit Generation

Rokuro Nishimura and Norio Sato

ISIJ International, **31,** 177 (1990)

The layer structure and composition of passive films formed on iron in borate and phosphate solutions at pH 8.42 and 11.50 have been investigated by means of cathodic reduction combined with ellipsometry and chemical analysis. Breakdown of the passive films has also been examined in 0.5 kmol/m^3 NaCl solution at a constant potential higher than a critical pitting potential in the same solution. It is found that the composition and breakdown of the passive films change with the potential of film formation, anion species and solution pH, while the film is always of two-layer structure consisting of a barrier layer in contact with the metal and a hydrated deposit layer next to the solution. The dependence of anion species and pH on the composition and breakdown of the films may be systematically explained in terms of an ion selective property of the passive films. Therefore it is suggested that the ion transport in the layers plays an important role in determining the passive film composition and the breakdown. (English)

Exchange Ratio Between the Protons of Surface Hydroxyl Groups on Manganese Dioxide and Zinc (II) Ions in Solution

N. Katayama, H. Tamura and R. Furuichi

Bunkeki Kagaku, **39,** 547-551 (1990)

When Zn(II) ions are adsorbed on MnO_2, protons are released from the surface of the MnO_2. The amounts of the released protons was measured by titration, and the adsorbed Zn(II) was determined by AAS. The ratio between the amounts of the released protons and adsorbed Zn(II) was obtained as a function of pH and the total concentration of added Zn(II). The ratio was about 1.1, independent of pH for 10^{-3} M added Zn(II) but increased with pH at 10^{-4} M Zn(II). The released H^+/adsorbed Zn(II) ratio was calculated from the stoichiometry and the equilibrium conditions of the adsorption reactions: Zn(II) ions react 1 and 2 acid surface hydroxyl groups on MnO_2 to form (1 : 1) and (1 : 2) surface complexes. The concentrations of the surface complexes are calculated from their stability constants, and the amounts of released propons and adsorbed Zn(II) are obstained from the concentrations of (1 : 1) and (1 : 2) complexes. Calculations show that the ratio increases with pH because the (1 : 2) complexes become predominant over the (1 : 1) complexes at higher pH values, but at higher Zn(II) concentrations, this ratio becomes independent of pH because the resulting high concentration of (1 : 2) complexes suppresses further (1 : 2) complex formation. The measured ratio of released H^+/adsorbed Zn(II) coincided well with the calculated values. (Japanese)

Characterization of the Acid-Base Properties of MnO_2 and Other Metal Oxide Samples in Aqueous Media

Hiroki Tamuran, Masaichi Nagayama
and Ryusaburo Furuichi

Progress in Batteries and Solar Cells,
Vol. 9, pp. 181-187 (1990)

The surface charge on MnO_2, Fe_3O_4, and TiO_2 samples in $NaNO_3$ solutions were measured as a function of pH by titration. The charge is formed by the acid-base dissociation of surface hydroxyl groups, the ion-exchange between H^+ and Na^+ ions and between OH^- and NO_3^-ions. The relationship between the surface charge and pH was characterized by a nonlinear least squares method with the Frumkin type equilibtium conditions, in which suppression of dissociation by formed charged sites is assumed. The established equilibrium constants fit the experimental data well and the acid-base properties of oxide samples, and PZC were quantitatively explained with these constants. (English)

Characterization of the Adsorption of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} Ions on an MnO_2 Sample

Hiroki Tamura, Noriaki Katayama, Masaichi Nagayama
and Ryusaburo Furuichi

Progress in Batteries and Solar Cells,
Vol. 9, pp. 188–195 (1990)

The amounts of adsorption of Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} ions on MnO_2 were examined as a function of pH and the concentrations of metal ions and MnO_2. The metal ions are adsorbed by forming surface complexes with acid hydroxyl groups on the metal oxides replacing one or two protons. The adsorption behavior was analyzed by fitting the Frumkin type equations, in which suppression of adsorption by the adsorbed metal ions is assumed. The established equilibrium constants explain well the measured adsorption isotherms. With these constants the concentrations of the surface complexes and the fraction of adsorbed metal ions were calculated as a function of pH for specified conditions. The calculations quantitatively show the affinity of metal ions and the ability of metal oxides for adsorption. (English)

Effect of $LaCrO_3$ Coating on the High Temperature Oxidation of Stainless Steels

Hidetaka Konno, Satoru Kitazaki and Ryusaburo Furuichi

Boshoku Gijutsu, **39,** 544 (1990)

Formation conditions for lanthanum chromium oxide, $LaCrO_3$, coating on SUS 304 and 430 stainless steels were determined and the effects of the coating on high temperature oxidation of the steels were examined. The coated steels showed excellent oxidation resistance at 1273 K in 0.20 atm H_2O-air and under cycle oxidation in air (20 h at 1173 K/4 h at room temperature). After the oxidation tests, small amounts of Cr_2O_3 and $(Mn, Fe)(Fe, Cr)_2O_4$ spinels were found under the coating but not on the coating, and the Cr_2O_3/spinel ratio (by XRD) was smaller than with the uncoated steels oxidized under similar conditions. Voids due to internal oxidation were also found in the outermost part of the coated steels. These findings suggest that the coating functions as a barrier preventing metal ions migrating outward, resulting in a low oxidation rate. (Japanese)

Formation of Perovskite Structure $La_{1-x}Ca_xCrO_3$ Films with Electrodeposition

H. Konno, M. Tokita and R. Furuichi

J. Electrochem. Soc., **137,** 361 (1990)

A method to from $La_{1-x}Ca_xCrO_3$ ($x=0$ to 0.2) films on Pt and Ni was reported as an accelerated brief communication. The method consists of the formation of precursor films, $(LaOH)_{1-x}Ca_xCrO_4$ nH_2O, on metals by cathodic deposition from chromate solutions containing La(III) and Ca(II) ions, and the pyrolysis of the precursor films above 700°C. (English)

Improvement of Anti-Oxidation Properties of Steels by Co-Diffusion Coating of Cr and Al

Liu Yu Xian, Toshio Narita and Tatsuo Ishikawa

Bulletin of the Faculty of Engineering Hokkaido
University. No. 152 (1990), 21

In order to improve anti-corrosion properties of carbon steels, diffusion-coating processes of Cr, Al, and their mixtures were investigated by using a pack-cementation method, where pure Cr and Fe–50 mass%Al alloy powders as well as their mixtures were used for vapor sources of Cr, Al and their mixtures. Diffusion layer thickness and concentration profilles were determined as functions of temperatures, diffusion times, and chemical composition of the mixtures for co-diffusion of Cr and Al.

Surface concentrations of 17 mass%Cr and 8 mass%Al were obtained when a mixture of 93Cr and 7 (Fe–50Al) powder was used, and this diffusion coating layer was indicated by a corrosion test to be highly protective against high temperature oxidation in air at 800°C. (Japanese)

Measurement of Residual Thermal Stress and Its Distribution on Silicon Nitride Ceramics Joined to Metals with Scanning Acoustic Microscopy

Toshio Narita, Kazumi Miura, Isao Ishikawa
and Tatsuo Ishikawa

J. Japan Inst. Metals, Vol. 54, No. 10 (1990),
pp. 1142-1146

Residual thermal stress on the ceramics joined to metals was determined with a reflection-type acoustic microscope. This report is concerned with an apparatus for measuring surface acoustic wave (SAW) propagation velocity and an analytical method for determining residual stress from the change in SAW velocity as well as the results obtained for the silicon nitride ceramics joined to stainless steel with Ni/W/Ni interlayers.

The maximum stress in the vicinity of the ceramic/metal interface, which was tension in nature, was estimated to be 400, 200, and 600 MPa for joints with 0.5 mm Ni (A), 1.25 mm Ni (B), and 2.0 mm Ni (C) interlayers. The stress decreased gradually with the distance from the ceramic/metal interface for the joint C, whereas for the joint A the stress profile was complex, showing a small compressive stress at a distance of 0.7 mm and a maximum tensile stress between 1 and 2 mm. For the joint B, the tensile stress was relatively low all over the ceramics. A four-point bending test at room temperature showed that joints A and C had a relatively low fracture strength, while the joint B had the highest strength of 230 MPa, because of low residual thermal stress.

It is proposed that the scanning acoustic microscope shows considerable promise for the non-destructive evaluation of the stress and stress distribution at the ceramic surface of ceramic/metal joints. (Japanese)

Joining of Fully Stabilized Zirconia Ceramics to Metals using Ag-Cu-Ti Solder and Ni-interlayers

Toshio Narita, Toshiki Mitsueda and Tatsuo Ishikawa

J. Japan Inst. Metals, Vol. 54, No. 3 (1990), pp. 321-327

A fully stabilized zirconia ceramics (FSZ) were joined to FSZ ceramics, chromium and nickel metals, and Kovar-alloy at 1123 K in vacuum using a Ag-Cu-Ti solder and with or without interlayers, which composed of Ni, Ni/W, and Ni/Kovar-alloy plates.

Fracture strengthes are 30 MPa for a FSZ/FSZ joint, 20-60 MPa for a FSZ/Cr joint, 82 MPa for a FSZ/(Ni/W)/Ni joint, 97 MPa for a FSZ(Ni/W)/Cr joint, 111 MPa for a FSZ/(Ni/Kover-alloy) /Cr joint, and 115 MPa for a FSZ/(Ni)/Kover-alloy joint. Compositional analysis revealed that titanium in the FSZ/FSZ and FSZ/Cr joint concentrated at the ceramic/metal interface. while in joints with interlayers almost titanium existed within a solder layer.

It was suggested for the FSZ/FSZ joint that titanium in the solder degraded significantly mechanical properties of the FSZ ceramics, dark-browned in color, resulting in low fracture strengthes of the joint. When FSZ ceramics were joined using interlayers, nickel dissolved into the solder reacted immediately with titanium and copper to form initially Ni-Ti and then Ni-Ti-Cu solid phases, reducing excess reaction between titanium and ceramics. This could be ascribed to strengthen the joints with nickel interlayers. (Japanese)

Reactions of Silicon-Nitride Ceramics with Ni

Toshiyuki Takashima, Tsuyoshi Yamamoto
and Toshio Narita

J. Ceram. Soc. Jpn. Inter. Ed. Vol. 98 [37–43] (1990)

The reaction between the silicon-nitride ceramics and nickel was studied in vacuum from 1373 to 1472 K for up to 176.4 ks. The reaction product was composed of two layers, one formed by the diffusion of silicon into nickel, and the other composed of additive oxides particles and nickel-silicon alloy.

The growth of the product layer followed the parabolic law with the following rate constants (Kp): $1.2 \times 10^{-13}\ \mathrm{m^2 \cdot s^{-1}}$ at 1372 K, $3.6 \times 10^{-13}\ \mathrm{m^2 \cdot s^{-1}}$ at 1423 K, and $1.7 \times 10^{-12}\ \mathrm{m^2 \cdot s^{-1}}$ at 1473 K.

The interdiffusion coefficients ($\tilde{D}$) obtained were of the orders of 10^{-15} to $10^{-14}\ \mathrm{m^2 \cdot s^{-1}}$ in the temperatures range studied.

These values were found to be one half to one fifth of the interdiffusion coefficients determined with a vapour solid diffusion couple of a nickel-plact and nickel-silicon alloy powder as diffusion source of silicon vapour. The activation energy for interdiffusion ($\hat{Q}$) was about $330\ \mathrm{kJ \cdot mol^{-1}}$, independent of the Si concentration.
(English)

Alumium-Chlorine Fuel Cell in High Temperature Chloride Melts

T. Ishikawa, T. Narita and S. Konda

Proc. of the Third China-Japan Molten Salt Chem.
and Tech. Bilateral Conf., p. 51-54 (1990)

In order to produce high-purity aluminum from aluminum scraps through electrowinning process in chloride melts, chlorination reaction of aluminum in an aluminum-chlorine fuel cell was investigated. The cell was constructed from a chlorine/graphite electrode as a cathode and aluminum metal as an anode in a mixture of $MgCl_2$ 25 mol%-NaCl 75 mol%. By separating the output voltage drop caused by chlorine reduction resistance from that by electrolytic resistance, the performance of the cell was investigated in terms of reaction resistance. For this purpose, the output voltage drops due to chlorine redution were determined at various kinds of electrodes with different hole sizes and numbers. The results show that the reaction resistance decreases with decrease in diameter of holes and have minimum values at about 3 mm hole. It also has a tendency to depending on the number of holes. The reaction zone for chlorine reduction is also discussed. (English)

Electrowinning of Liquid Magnesium by Using a Stacked-Type Bipolar Electrode Cell

T. Ishikawa, T. Narita and S. Konda

Proc. 7th Int. Sympo. MOLTEN SALTS PV90-17,
p. 600-610 (1990)

This paper describes the design and construction of a stacked-type bipolar electrode cell for electrowinning liquid magnesium from chloride melts. The laboratory-scale electrolysis was carried out with a bipolar electrode-type cell operated at 50 A current at about 750°C. During electrolysis the metallic particles of magnesium move to the melt surface together with gas bubbles of chlorine. The experimental results are discussed considering the collection of magnesium particles from chlorine gas and the circulation of chloride melt. (English)

Electrodeposition of Gallium on Gallium Electrode in Bayer Solution

Hirobumi Mizuno, Takeshi Toyoda, Takeshi Sasaki
and Tatsuo Ishikawa

Bulletin of the Faculty of Engineering Hokkaido
University No. 152 p. 31 (1990)

In order to remove materials coexisting in Bayer solution which may restrain the electrodeposition of gallium on a gallium electrode, Bayer solution was cooled at various temperatures with or without sodium salts of coexisting materials as a seed for crystallization.

The concentrations of vanadium, arsenic, and phosphorous decrease to 1/5～1/2 of original concentrations by cooling at -20°C for about one week. The electrolysis by using a gallium electrode in the Bayer solution as treated at -20°C achieves the electrodepositon of gallium at lower potential than -2.1 V vs. Ag-AgCl. The largest current efficiency as 0.06～0.80% is observed at -2.1 V electrolysis. (Japanese)

In-situ Measurement of Metal Surfaces by Using Piezoelectric Properties

Masahiro Seo

Report of Tech. Meeting of Corr. Eng. Div.. Soc. Master
Sci. Japan, No. 158, Vol. 29, Part 5, 46-54 (1990)

This article introduced the principle, features and application of piezoelectric response method for detecting sensitivity a small change in surface stress of metal electrode produced by a potential modulation. The piezoelectric element attached to the back side of metal foil electrode via dielectric film for electric isolation is capable of transducing the surface stress change to the piezoelectric signal.

By taking the typical examples of experimental data, it is shown that the fundamental knowledge of electrode interface such as potential of zero charge, specific adsorption of electrolyte anions, and initial film formation process is obtained from this technique. (Japanase)

Piezoelectric Response to Specific Adsorption of Chloride Ions on Gold Electrode

Xiang Chung Jiang, Masahiro Seo and Norio Sato

J. Electrochem. Soc., **137**, 3804-2808 (1990)

The specific adsorption of Cl^- ions on gold electrode was investigated by a piezoelectric technique combined with admittance measurement. The specific adsorption contributed greatly to the piezoelectric signal produced by a potential modulation technique. Several parameters of the specific adsorption such as electrosorption valency, γ, and surface excess, Γ_{ad} were evaluated from the piezoelectric signals. These results indicated that the specific adsorption of Cl^- ions took place accompanying a partial charge transfer and induced the structural change of the electric double layer leading to the formation of a surface adsorption compound. (English)

Measurement of Absorption of Hydrogen and Deuterium into Palladium during Electrolysis by a Quartz Crystal Microbalance

Lars Grasjo and Masahiro Seo

J. Electroanal. Chem., **296**, 233–239 (1990)

The in-situ QCM-technique is applied to the palladium-hydrogen or palladium-deuterium system. The amount of hydrogen (deuterium) absorbed into the palladium is controlled by changing the potential applied to the palladium. The absorbed hydrogen (deuterium) would create the stress which gives rise to significant deviation from Sauerbrey's equation. The apparent relation between changes in mass and resonance frequency is reported for the α- and β-phase of the Pd-H(D) system. The stress factors influencing the QCM results are discussed. (English)

Oxidation-State Changes of Molecules Irreversibly Adsorbed on Electrode Surfaces as Monitored by in situ Fourier Transfom Infrared Reflection Absorption Spectroscopy

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Langmuir **6,** 1234–1237 (1990)

In situ Fourier transform infrared reflection adsorption spectroscopy has been used to monitor the changes in the vibrational properties of 2,5-dihydroxythiophenol (DHT) irreversibly adsorbed on polycrystalline Au as a function of the applied potential. The results obtained have indicated that the normalized difference spectra of DHT in its oxidized state exhibit features consistent with the formation of the quinone derivative of the compound, benzoquinonethiol (BQT), in agreement with the suggestions put forward earlier in the literature on the basis of other measurements. Strong similarities were also found between the normalized difference spectra of adsorbed and solution-phase BQT. The relatively large intensity of the signals observed for the adsorbed species has provided strong evidence that both DHT and BHQ are adsorbed on Au with the molecular plane forming a small rather than large angle with respect to the normal to the surface. (English)

Study on the Preparation of Ferric Oxide Powders and their Reactivity in Solid State Reaction

Ryusaburo Furuichi

Rept. Asahi Glass Found., **56,** 355-364 (1990)

The effect of foreign metal ions, Me=Cu^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+}, Ni^{2+}, Al^{3+}, and Cr^{3+}, added to Fe(III)-hydroxides on the formation of α-Fe_2O_3 was studied with DTA, TG and XRD. The addition of Me was carried out by three procedures; co-precipitation, gel-mixing and mortar-mixing. The hydroxide without Me showed an exothermic DTA peak at Tc=414°C due to the crystallization to α-Fe_2O_3. The co-precipitated samples indicated that the crystallization temperature Tc shifted to higher temperatures at 527-559 °C. The gel-mixed samples gave Tc values similar to those for the co-precipitated hydroxides. It was suggested that the mortar-mixing procedure results in an inhomogeneous interaction between Fe(III)-hydroxide and Me-oxide particles.

The catalytic effect of α-Fe_2O_3 on thermal decomposition of $KClO_4$ was studied to compare the reactivity of the oxides prepared from $FeC_2O_4\cdot 2H_2O$ by heating it at different temperatures between 500 and 1000°C. By the addition of the oxide, the solid phase decomposition of the perchlorate was accelerated to proceed at lower temperatures by 110-150°C, and the amount of the solid phase decomposition increased from 3% to 6.5-39%, and the activation energy decreased from 78.4 kcal/mol to 53.6-60.8 kcal/mol. The catalytic effect was found to depend on the preparation temperature of α-Fe_2O_3 and the mixing ratio of the oxide to the perchlorate. (Japanese)

Migration Behavior of Palladium in UO_2

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JAERI-M 90-113

Palladium (Pd) is one of the interesting fission products in both HRGR and LWR fuel technologies. It is easily released from UO_2 kernels in HRGR coated fuel particles and reacts with SiC coating layer. Also, Pd is one of the metal fission products composing the metallic precipitate in irradiated UO_2, which is undissolvable residue in the reprocessing of LWR fuel. The present research is concerning the Pd migration in UO_2 which was studied as follows. UO_2 containing Pd and Pd+Mo was prepared, and heat-treated at 1800°C, followed by an electron probe microanalysis (EPMA) and a ceramography in order to observe growth of the Pd precipitates. Furthermore. Pd diffusion in UO_2 was studied in the method that Pd was physically vapour-deposited in the surface of UO_2, and the diffusion couples of UO_2 were annealed at 1400°C, followed by observation by EPMA for determination of Pd diffusion coefficients. It was concluded in this study that number density of the Pd precipitate in UO_2 decreased with heating time, where as mean diameter of the precipitate increased. Influence of Mo addition on growth of the precipitate was not recognized. Also, the composition of Pd and Mo measured in the precipitate was different from the equilibrium one of the Pd-Mo phase diagram. In the diffusion experiment Pd was detected at the point of 400 μm depth from the surface. The diffusion coefficient obtained in this study was about 10^{-10} cm^2/s. (Japanese)

Present Situation of Research and Development of Radioactive Waste Disposal

Seichi Sato

Bull. Nucl. Safety Res. Ass. No. 114, 12～16, (1990)

Present situation on high-level radioactive waste disposal in European countries were shortly summarized. It includes feasibility studies, procedures for safty analysis of disposal system and scientific and technical problems to be studied. (English)

Identification and Assessment of radiation Induced Degradation

Mechanism: Preliminary Methodical and Methodological Consideration

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LAEA/NENF/NF-90/6, IAEA. VIENNA 1～15 (1990)

It is clearly recognized that radiation may be as important factor in the degradation of properties for a range of materials and components being used in the back-end of the fuel cycle. By discussion among the experts involved it was possible to prepare a list of radiation-assisted degradation mechanisms that would likely affect these materials/components. The results are given in a Table. The first column lists the components into nine categories. However, it must be noted that for certain categories the components may be further subdivided into sub-categories which could be widely different in composition. The main degradation mechanisms are listed in the table, and their relevance to individual components are indicated with a cross.

Since the importance of each radiation-assisted degradation mechanism depends on the individual component/material, it is nacessary to make a judgement on the magnitude of the effect. This was achieved by ranking the radiation effect according to four (4) categories: (4). Category (1) indicated that radiation has a large effect on the degradation mechanism, category (2) a moderate effect, category (3) a small or insignificant effect, and category (4) indicates that it is not clear whether there is, in fact, a radiation effect at all. It seems probable, however, that most category (4) rankings will, upon detailed study, emerge as category (3) since any major radiation-induced changes would likely to have been discovered very early. (English)

Behavior of Helium Release from Simulated Radioactive Waste Glasses

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Journal of Nuclear Science and Technology, **27** [4].
pp. 343∼349 (1990)

Rates of He release from two kinds of simulated high-level radioactive waste glasses were measured in the temperature range from 573 to 753 k by a mass spectrometric method. Diffusion coefficoent of He in the glasses were determined from the factional release data. The diffusion coefficients were given as a function of temperature by equation :

$D/(m^2 \cdot s^{-1}) = 2.3 \times 10^{-6} \exp(-7.1 \pm 2.1\ k/RT)$ for P0798 glass

$= 9.8 \times 10^{-7} \exp(-60.2 \pm 2.1\ k/RT)$ for P0504 glass.

In addition, solubilities of He in the glass were determined from the measurement of the total amount of released He and found to be

$S/(atoms/m^3) = 2.0 \times 10^{22}$ for P0798 glass,

$= 2.2 \times 10^{22}$ for P0504 glass

at 698 K and 1.7×10^5 Pa He.

The diffusivities and solubilities of He in the glasses were, respectively, several and an order of magnitude lower than silica, alkali silicate and Pyrex glasses, which properties are notable for the radioavtive waste glasses. (English)

Preparative Method for Fabricating a Microelectrode Ensemble: Electrochemical Response of Microporous Aluminum Anodic Oxide Film Modified Gold Electrode

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Anal. Chem., **62,** 652 (1990)

A novel method for the preparation of an ultramicroelectrode ensemble is demonstrated. At the initial stage of barrier layer removal following the vacuum evaporation of Au into micropores of aluminum anodic oxide films, sigmoidal CVs, which are expected for the microdisk electrode, were observed. When Au was deposited with a deposition angle of 30°, to avoid filling the micropores with Au, the CV of a thin layer cell showing exhaustive redox behavior with a peak separation of 30 mV and symmetric waves, was observed. (English)