ANNUAL REPORT

1988

CORROSION RESEARCH

Materials Science and Engineering

published
by
THE CORROSION RESEARCH GROUP

FACULTY OF ENGINEERING
HOKKAIDO UNIVERSITY

NO. 17 DECEMBER 1988

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ELECTROCHEMISTRY LABORATORY

Prof. Dr. N. Sato, Assoc. Prof. Dr. M. Seo,
Assoc. Prof. Dr. T. Ohtsuka, Mr. K. Azumi
and Miss. J. Fujiwara

Students

X. C. Jiang, L. Grasjo, H. Bogaki, K. Aotsuka, I. Takeda,
T. Sakamoto, K. Araki, I. Sawamura, T. Sonoda,
T. Fujita and S. Ishiguro

The research activity of the laboratory continues to be directed towards a better understanding of the properties of interfacial phase on the surfaces of metals in relation to the corrosion and passivation of metals and to the interfacial electrochemistry.

Transient Photocurrent for the Passivated Iron Electrode

The transient photocurrent was measured for the iron electrodes passivated in neutral borate and phosphate solutions. A simulation was made to explain the transient behaviour of the photocurrent assuming an equivalent circuit with the generation of a photo-induced free carrier in the n-type passive film. From the simulation electronic property of the passive film, recombination rate of photo-induced free carrier, and the density of the surface states were evaluated.

Laser Raman Spectroscopy for the Rust Layer Identification

The initial rust layer formed on the low-alloy steels at 20~50°C was investigated by in-situ laser Raman spectroscopy. The aqueous droplet containing variuos salts induces a rapid rust formation. The Raman spectra from the rust indicate the initial formation of γ-FeOOH, and the slow modification to γ-Fe_2O_3 and Fe_3O_4. The rust formed by pure water droplet shows relatively strong Raman peaks of γ-FeOOH even after exprosure for 10d. The rust of weathering steel with relatively high concentration of P is composed mainly of γ-Fe_2O_3 and the Raman peaks of Fe_3O_4 in the rust remains a low level.

Piezo-electric Response to Metal Electrodes

The piezo-electric detection was applied to nickel electrode in acidic sulfate solution to measure the potential of zero charge (pzc) and to investigate the active/passive transition. The piezo-electric signals contain two terms of surface electric charge and adsorption of electrolyte ions. The frequency analysis of piezo-electric signals could separate the above two terms. The competitive processes of active dissolution and passivation were discussed from the potential dependence of adsorption term in piezo-electric signals.

Furthermore, the specific adsorption of chloride ions on gold electrode was investigated by combining the piezo-electric technique with an admittance measurement. The specific adsorption induced a large increase of the piezo-electric signals before a partial charge transfer. Above critical potential, however, the signals decreased with increasing electrode potential because of the partial charge transfer and/or the deep penetration of adsorbed chloride ions in the inner Helmholtz layer. The structual change of electric double layer due to the specific adsorption was dicussed from the evaluated values of parameters influencing on adsorption.

Metal Oxide Films Prepared with MOCVD

Metal oxide film of Cr_2O_3 was prepared on aluminum substrate with a metal organic chemical vapor deposition (MOCVD) to improve the pitting resistance of aluminum. The depth-composition profile of the Cr_2O_3/Al system was measured by Auger electron spectroscopy combined with argon-ion sputter-etching technique. Laser Raman spectroscopy has revealed an amorphous structure of the Cr_2O_3 film. It is found that the pitting potential of aluminum due to the surface coating with Cr_2O_3 film shifts by 1.5 V to the more anodic direction in comparison with bare aluminum.

Application of Quartz Crystal Microbalance to Corrosion

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 investigate the anodic oxidation process of copper in pH 8.4 borate solution. The real current measured during anodic oxidation at a constant potential in the passive region was compared with the apparent current calculated from the frequency change in QCM. It was shown that the dissolution rate of cupric ions through the passive film into solution and the uptake rate of oxygen in the film could be separately evaluated from the comparison with the real and apparent currents at the high potential where the dissolution of cuprous ions was negligibly small.

Electroluminescence from Silicon Electrode

Electroluminescence (EL) was detected from single crystal Si(100) with p-type during anodic oxidation in ethylene glycol solution containing NO_3^- ions as an electrolyte to investigate the effect of water and chloride ions contained in the solution on EL and anodic oxidation. The broad EL spectra with two peaks at about 350 nm and 670 nm were observed at 80 V under the galvanostatic condition. The addition of Water to the solution reduced the both two peak intensities, whereas the addition of chloride ions enhanced only the peak intensity of 670 nm. The defective structure of silica film formed on Si during anodic oxidation was discussed on bases of these EL results.

Spectro-Electrochemical Characterization of Polypyrrole Film

The polypyrrole film electrochemically formed on Pt electrode in aqueous solution was measured by ellipsometry and laser Raman spectroscopy. From the ellipsometric measurement, the growth of film with a refractive index of $n=(1.43-1.55)-(0.51-0.53)i$ was observed and the optical change to a film of refractive index of $n=1.85-0.09i$ due to cathodic reduction at -0.6 V was detected. There was also large difference between the Raman spectra of oxidized and reduced forms of the polypyrrole.

Surface Coating of the Langmuir-Blodgett Film

A very thin surface coating film with 10, 12-tricosadiynoic acid was made on a planium plate and a gold sputtered glass plate by using the LB technique. The surface film deposited on the substrates was then polymerized by irradiation of UV light. Impedance, electrochemical polarization and Raman spectroscopy were used in order to examine the properties of the surface film. The resonance Raman scattering was proved to be available for investigation of the very thin surface organic film one-or two-monolayer thick.

Other Activities

In 1988, Assoc. Prof. M. Seo visited Professor J. C. Eriksson at the Royal Institute of Technology in Stockholm and Dr. C. Leygraf at the Swedish Corrosion Institute on June 9–10 for a Japan-Sweden collaborative research and also visited Professor M. Froment and his group at University of Paris IV, France on June 13. Afterward, Assoc. Prof. M. Seo attended the 4th International Fischer Symposium on Electrochemical Phase Formation and Dissolution held in Karlsruhe, FRG on June 14～18 and presented a paper entitled "Piezoelectric Detection of Underpotential Deposition of Copper on Gold in Sulfuric and Perchloric Acid Solutions".

Professor N. Sato visited the Beijing University of Science and Technology, the Institute of Corrosion and Protection of Metals and the Shanghai Institute of Metallurgy, China on September 11～25.

Assoc. Prof. M. Seo visited Professor K. L. Tan and Dr. G. Hultquist at National University of Singapore, Singapore on November 10～20 for JSPS-NUS Scientific Cooperation on Surface Physico-chemical Study of Metal-Hydrogen-Oxygen-Water Systems and presented two lectures entitled "Some New Analytical Technique for Study of Solid Surfaces" and "Fundamental Approach to Corrosion Protection". Mr. L. Grasjo, PhD Student at the Royal Institute of technology, has joined this laboratory since January, 1988 to conduct an electrochemical study of Pd and Cu combined with a quartz crystal microbalance.

The following scientists from over the sea paid the short visit to this laboratory in this year of 1988 : Dr. D. Feron from Atomic Energy Laboratory, Cherbourg, France on April 28, Dr. M. Graham from National Research Council, Canada on May 30, Professor J. C. Eriksson from the Royal Institute of Technology, Stockholm, Sweden on May 30～31 and Dr. G. Hultquist from National University of Singapore, Singapore (on leave from the Royal Institute of Technology, Stockholm, Sweden) on September 6～10.

Oral Presentation

Raman spectroscopy for the Corrosion Product of Metallic Materials; T. Ohtsuka: Symposium on New Developments of Raman Spectroscopy of the Spectroscopic Soc. of Jpn., Jan., 1988

Change in Photoacoustic Signal during Cathodic Reduction of Passive Films on Iron and Copper; M. Seo, X. C. Jiang and N. Sato: The 14th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan. 1988

The Effect of UPD of Copper on PZC of Gold Electrode; X. C. Jiang, M. Seo and N. Sato: *ibid.*, Jan., 1988

Application of QCM to Corrosion Research; M. Seo, Y. Haga and N. Sato: The 23rd Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1988

On Application of Raman Spectroscopy for the Corrosion Study; T. Ohtsuka and N. Sato: *ibid.*, Jan., 1988

Preparation of Multilayers of Metal Thin Oxide Films with MOCVD and Depth-composition Profiles; K. Takemasa, M. Seo and N. Sato: The 1987 Winter Meeting of the Hokkaido Section of the Jpn. Soc. for Analytical Chem. and Jpn. Chem. Soc., Feb., 1988

Ion Gate of Polypyrrole Membrane Coated on Teflon Filter; T. Bogaki, T. Ohtsuka and N. Sato: *ibid.*, Feb., 1988

Study of UPD on Gold Electrode by Piezoelectric Response of Surface Stress Change; M. Seo, X. C. Jiang and N. Sato: The 55th Meeting of Electrochem. Soc. Jpn., April, 1988

Electrochemical Behaviors and Surface Composition of Fe-Cr Alloys in High-Temperature Solution; M. Seo, K. Sakamoto and N. Sato: *ibid.*, April, 1988

Photoacoustic Study of Cathodic Reduction of Anodic Oxide Films on Iron and Copper; X. C. Jiang, M. Seo and N. Sato: '88 Spring Meeting of the Japn. Soc. Corros. Eng., May, 1988

Application of QCM to Study on Atmospheric Corrosion of Cu/H_2S System; M. Seo, Y. Haga and N. Sato: *ibid.*, May, 1988

Potential Region for Crack Susceptibility and Film Composition of Stainless steel with Small Punch Test under High Temperature-High Pressure and Heavy Radiation Environments; S. Misawa, M. Saito, H. Sugawara, T. Ohtsuka and M. Seo: *ibid.*, May, 1988

Direct Measurement of the Electric Resistance of the Passive Films formed on Iron and Titanium Electrodes in Neutral Solution by using the Contact Electrode; K. Azumi, T. Ohtsuka and N. Sato: *ibid.*, May 1988

Impedance of Cobalt Electrode Anodically oxidized in Neutral Borate Solution; T. Ohtsuka and N. Sato: *ibid.*, May 1988

Breakdown and Repair of Passive Films; M. Seo: The 44th Tech. Meeting of Corr. Eng. Div., The Soc. of Mater. Sci. Jpn., May, 1988

Piezoelectric Detection of Underpotential Deposition of Copper on Gold in Sulfuric and Perchloric Acid Solutions: M. Seo, X. C. Jiang and N. Sato: The 4th International Fischer Symposium on Electrochemical Phase Formation and Dissolution, Karlsruhe, FRG, June, 1988

Piezoelectric Detection of Surface Stress Change of Metal Electrode; M. Seo: Seminar at University of Paris IV, France, June, 1988

Raman Spectroscopy of metal Oxides and Apparatus for High-Temperature in situ Laser Raman Spectroscopy in Aqueous Environments; T. Ohtsuka, M. Ishibashi and K. Yoshikawa: NATO Advanced Study Institute "Spectroscopic and Diffraction Technique in Interfacial Electrochemistry", Canary Islands, Spain, Sept., 1988

Ionic Selectivity of Electrochemically Polymerized Polypyrrole Membrane With Various Dopant Anions; T. Bogaki, T. Ohtsuka and N. Sato: The 1988 Autumn Meeting of Electrochem. Soc. Jpn., Sept., 1988

Potential Dependence of Anodic Oxide Film on Tungsten by in-situ

Raman and Infrared Spectroscopy; T. Ohtsuka, N. Goto, K. Junimatsu and N. Sato: The 57th Autumn Meeting of Jpn. Chem. Soc., Sept., 1988

Some New Analytical Technique for Study of Solid Surfaces; M. Seo: Seminar at National University of Singapore, Singapore, Nov., 1988

Fundamental Approach to Corrosion Protection; M. Seo: *ibid.*, Nov., 1988

NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. T. Morozumi, Assoc. Prof. Dr. Ohashi,
Dr. T. Mizuno, Dr. M. Moriya, Mr. K. Hirohara,
and Mrs. N. Ochiai

Students

M. Takada, S. Miyashita, N. Mura, O. Ando,
T. Oikoshi, S. Sibata and T. Fukuoka

The laboratory is concerned with investigations on corrosion of metallic materials used in nuclear industry, characterizations of iron rust components, development and improvement of hydrogen reservoir alloys, and elucidation of the mechanism of pitting corrosion.

(1) Corrosion of SUS304 stainless steel was electrochemically investigated in aqueous solutions of organic chelating reagents which are used for decontamination of primary water coolant circuits of nuclear reactors.

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

(3) The dissolution rates 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 in the decontamination reagents.

(4) Structural changes of the $FeTi_{1.1}$ hydrogen reservoir alloy by thermal treatment and by absorption and desorption of hydrogen were investigated. Changes in lattice parameters and Mössbauer spectra were determined as a function of annealing and absorption and desorption cycles of hydrogen.

(5) Pitting corrosion of iron was investigated in buffered solutions by in-site radiotracer measurements. Growth of pits was discussed by chloride ion accumulation and time variations in current in pits. The pitting process is explained by the proposed two step theory.

(6) 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.

Professor Y. K. Yoon from the Korea Advanced Institute of Science and Technology visited our laboratory on July 25, 1988, and gave a lecture on "The Present Status of Development of Nuclear Power in Korea" to the Hokkaido Section of the Atomic Energy Society of Japan.

Oral Presentations

A Relationship between Plating Thickness and Anti-Pulverization Characterization of Electroless Copper Plated Fe-Ti Alloy ; J. Kitabuki, T. Mizuno and T. Morozumi : The 1988 Winter Meeting of the Hokkaido Sections of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, Feb., 1988.

Determination of Valence State of Iron in Magnetite by Mössbauer Spectroscopy ; T. Kozaki, H. Ohashi and T. Morozumi : *ibid.*, Feb., 1988.

Dissolution Behavior of Magnetite in EDTA Solutions ; H. Ohashi, T. Kozaki, N. Kosai and T. Morozumi : *ibid.*, Feb., 1988.

A Study of Pulverization Processes of Fe-Ti Hydrogen Storage Alloy by Acoustic Emission Detection Method ; T. Mizuno, J. Kitabuki, Y. Hayashi and T. Morozumi : The Joint Meeting of the Hokkaido Sections of the Japan Institute of Metals and the Japan Iron and Steel Institute, June, 1988.

The Relationship between Plating Thickness of Fe-Ti hydrogen Storage Alloy and Its Pulverization Process ; T. Morozumi, T. Mizuno, J. Kitabuki and Y. Hayashi : *ibid.*, June, 1988.

Determination of Nonstoichiometry of Magnetite by Mössbauer Spectroscopy ; H. Ohashi, T. Kozaki and T. Morozumi : The 37 Annual Meeting of the Japan Society for Analytical Chemistry, Sept., 1988.

Dissolution Behavior of Magnetite in Relation to Its Nonstoichiometry; H. Ohashi, T. Kozaki and T. Morozumi: The 1988 Fall Meeting of the Atomic Energy Society of Japan, Oct., 1988.

Migration of Noble Metal Fission Products in UO_2 — Observation of Pd Distribution; H. Ohashi, M. Takada, T. Morozumi, T. Ogawa, K. Fukuda and H. Murakami: The 6th Meeting of the Hokkaido Section of the Atomic Energy Society of Japan, Dec., 1988.

Crud Formation and Transformation in Reactor Environments; H. Ohashi and T. Morozumi: *ibid.*, Dec., 1988.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Prof. Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno
and Miss A. Akazawa

Students

T. Oda, S. Kitazaki, N. Wakabayashi, M. Yamaki,
S. Tamura, M. Tokita and K. Watanabe

Drs. Takahashi and Konno visited VG Co., England, in Feb. 1988 to supervise the manufacture of our new ESCA apparatus (ESCALAB MkII-MICROLAB MkIII). The machine arrived at our laboratory in March, and the whole year was spent for setting up and adjustment of the instrument. Dr. Tamura was invited to give a lectrure at the IBA Workshop on Measurements on Battery Materials, Atlanta, in May 1988, he also joined the 173rd ECS Meeting subsequently held in the same city. Dr. Tamura joined the 6th International Conference on Surface and Colloid Science, Hakone, June 1988. Prof. Furuichi went to Israel for the 10th ICTA, Jerusalem, in Aug. 1988. The Hokkaido section of the Surface Finishing Society of Japan was established, and this was celebrated in Dec. 1988. The office will be in our laboratory and start work from Jan. 1989.

The research programs in our laboratory are:

(1) Reaction between metal oxide powders.

The effect of the mixing ratio of oxides on the powder reaction rates was examined for Fe_2O_3-MgO and Fe_2O_3-ZnO systems. The rate of reaction for the V_2O_5-Fe_2O_3 system was measured to check the effect of mixing method on the oxides.

(2) Characterization of acid-base properties of metal oxides.

The acid-base properties of MnO_2, Fe_2O_3, Al_2O_3, and TiO_2 were examined by titration. The acid-base nature of the oxides is caused by surface hydroxyl groups. The equilibrium constants for the dissociation of hydroxyl groups were determined by considering that the dissociation is suppressed by charged sites formed by the dissociation. The values can be used to characterize metal oxides as corrosion products or industrial materials, e. g., solid electrolytes, ion-exchangers, catalysts, etc.

(3) Characterization of ion-adsorption behavior on metal oxides.

Adsorption behavior of Co^{2+} ions on MnO_2 was examined. The adsorption is due to the formation of surface complexes between Co^{2+} and the surface hydroxyl groups on MnO_2. The equilibrium constants for the surface-complex formation were determined by considering that the reaction is suppressed by the formed surface complexes. The values of the constants were compared with those for Co^{2+}-magnetite, Zn^{2+}–MnO_2, and Cu^{2+}–MnO_2 complexes. Quantitative evaluation of the performance of metal oxides as inorganic ion-exchangers can be made by equilibrium calculations.

(4) Formation and deterioration of composite oxide films on aluminum.

Composite oxide films were formed by anodizing aluminum covered with a hydrous oxide, and were examined by electrochemical measurements and electron microscopy. The composite oxide was found to consist of two layers. The crystalline oxide layer contained 'voids' which causes a deterioration of oxide on open circuit in water. The deterioration was correlated with the distribution of voids in the oxide.

(5) Anodizing of Cu–Al and Si–Al alloys.

Cu–Al and Si–Al alloys were anodized in a sulfuric acid solution to form porous oxide films. The structure and formation behavior of the oxide film were examined as functions of the content of alloy element (Cu or Al) and anodizing condition.

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

A method utilizing cathodic deposition to form perovskite type lanthanum chromium oxide ($LaCrO_3$) films on metals was developed. The $LaCrO_3$ is electron conductive and resistant to oxidation at elevated temperatures. The project continues, and aims to produce $La_{1-x}M_xCrO_3$ (M=Ca, Sr, etc.) films which are electron conductive at room temperature and more useful as high temperature materials. Further, the developed method was found to be applicable to the synthesis of $La_{1-x}M_xCrO_3$ powder with lower energy consumption than conventional methods. Establishing a method for powder production is also planned.

(7) High temperature oxidation of stainless steels in H_2O/O_2 atmospheres and their protection by reactive element-chromium composite coatings.

A large amount of data was accumulated for oxidation of type 430 and 304 stainless steels at 1173-1373 K in 0.03-0.20 atm H_2O—0.165 atm O_2—N_2 atmospheres. It was found that $LaCrO_3$ is a good coating material to protect type 430 and 304 stainless steels from high temperature oxidation. The coating showed marked oxidation resistance at 1273 K in air containing 20% water vapor, and no spallation was observed in air after 20 thermal cycles of 20 h heating at 1173 K and cooling to room temperature. The project is now progressing to try to understand the mechanism of protection by the coating.

Oral Presentations

Effects of Current Density on the Formation of Anodic Oxide Films on Al/Si Alloy in a Sulfuric Acid Solution ; S. Hashimoto, H. Takahashi and R. Furuichi : 14th Meeting of Hokkaido Section of the Electrochemical Society of Japan, Jan., 1988.

Statistical Evaluation of High Temperature Oxidation Behavior of Stainless Steels in Water Vapor/Oxygen Atmospheres ; H. Konno, S. Kitazaki, R. Furuichi and I. Saeki : 23rd Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1988.

Determination of Acid-Base Dissociation Constants of Surface Hydroxyl Groups on MnO_2; T. Oda, H. Tamura and R. Furuichi: 1988 Winter Meeting of the Hokkaido Sections of Japan Society for Analytical Chemistry and Chemical Society of Japan, Feb., 1988.

Determination of Stability Constants of Cu^{2+}-MnO_2 Surface Complexes; T. Tatsumi, H. Tamura and R. Furuichi: *ibid.*

Adsorption-Desorption Behavior of Impurity Metal Ions on Battery MnO_2 in NH_4Cl Solutions; N. Katayama, H. Tamura and R. Furuichi: *ibid.*

Study on the Characterization of Metal Oxide/Aqueous Solution Systems; H. Tamura: Lecture for the Hokkaido Analytical Chemistry Award, Feb., 1988.

Structure of Oxide Films Formed on Aluminum; H. Takahashi: 77th Annual Meeting of the Metal Finishing Society of Japan, Mar., 1988.

Measurements of the Ratio of Zn^{2+}-H^+ exchange on MnO_2 Surfaces by Titration; N. Katayama, H. Tamura and R. Furuichi: 56th Spring Meeting of Japan Chemical Society, Apr., 1988.

High Temperature Oxidation Behavior of Stainless Steels in Water Vapor/Oxygen Mixed Atmospheres; H. Konno, S. Kitazaki and R. Furuichi: FUSHOKU-BOSHOKU '88, May, 1988.

Adsorption of Metallic Impurities on MnO_2; H. Tamura and M. Nagayama: Invited Lecture for IBA Workshop on Measurements on Battery Materials, Atlanta (U. S. A.), May, 1988.

Characterization of the Adsorption of Metal Ions on MnO_2; H. Tamura, N. Katayama, M. Nagayama and R. Furuichi: 173rd Meeting of the Electrochemical Society, Atlanta (U. S. A.), May, 1988.

Formulation of Iostherms for Cation Adsorption on Metal Oxides in Terms of the Stability Constants of Surface Complexes; H. Tamura, N. Katayama and R. Furuichi: 6th International Conference on Surface and Colloid Science, Hakone, Jun., 1988.

Characterization of Acid-Base Behavior of Metal Oxide/Aqueous Solution Interfaces; H. Tamura: Invited Lecture for the 7th Lilac Seminar Sponsored by the Hokkaido Section of Electrochemical Society of Japan, Jun., 1988.

Acid-Dissociation Characteristics of the Surface of Graphite Powders for Batteries; T. Oda, H. Tamura and R. Furuichi: 1988 Summer Meeting of the Hokkaido Sections of Chemical Society of Japan and Japan Society for Analytical Chemistry, Jul., 1988.

Effects of Si Content in Al/Si Casting Alloys on the Formation of Anodic Oxide Films in a Sulfuric Acid Solution; H. Takahashi, S. Hashimoto, K. Watanabe and R. Furuichi: *ibid.*

Ylide Metal Complexes (8). XPS Study on Tellurium Complexes of Methylenetriphenylphosphorane; H. Konno and Y. Yamamoto: *ibid.*

DTA Study on α-Fe_2O_3 Formation from Fe(III)-Hydroxides Containing Foreign Metallic Ions; R. Furuichi, M. Hachiya and T. Ishii: 9th International Congress on Thermal Analysis.

Determination of Stability Constants of Metal Ion-Metal Oxide Surface Complexes —Characterization of Equilibria for Ion Exchange and Adsorption—; H. Tamura, N. Katayama and R. Furuichi: 37th Meeting of Japan Society for Analytical Chemistry, Sept., 1988.

Effects of Structure of Aluminum Hydroxide Films on the Field-Assisted Dehydration; H. Takahashi and R. Furuichi: *ibid.*

Improving Oxidation Resistance of Stainless Steels with Lanthanum Chromite Coatings; H. Konno, S. Kitazaki, M. Tokita and R. Furuichi: 35th Annual Symposium on Corrosion and Protection, Oct., 1988.

Formation of $LaCrO_3$ Film by Electrolysis; H. Konno, M. Tokita, S. Kitazaki and R. Furuichi: 78th Meeting of Metal Finishing Soc. Japan, Oct., 1988.

On the Anodizing of Al/Si Casting Alloys in Sulfuric Acid Solution; H. Takahashi, S. Hashimoto, K. Watanabe and R. Furuichi: *ibid.*

Mechanism on the Formation of Composite Oxide Films on Aluminum; H. Takahashi: Special Seminar at Eruna Inc., Oct., 1988.

Role of Crystalline Structure of Hydroxide Films on the Formation of Composite Oxide Films on Aluminum; H. Takahashi:

Special Seminar Sponsored by Light Metal Foundation, Nov., 1988.

Aluminum Anodic Oxide Films and Functional Surfaces; H. Takahashi: Memorial Lecture at Foundation of Hokkaido Section of Surface Finishing Society of Japan, Dec., 1988.

ELECTROMETALLURGY LABORATORY

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

Students

K. Miura, S. Kawaziri, H. Takahashi, A. Hori, N. Yokoyama,
S. Ando, S. Ohe, Y. Shibata, Y. Mizuta,
M. Yamamoto and T. Yamamoto

Professor Ishikawa and Mr. Konda attended The Second Japan-China Bilateral Symposium on Molten Salt Chemistry and Technology which was held in Yokohama, Japan in Nov. 7～10, 1988. Professor Ishikawa, Associate Professor Narita and Mr. Miura attended International Meeting on Advanced Materials which was held in Tokyo, Japan in May 30-June 3, 1988. Dr. Sasaki left to spend his sabbatical period in Case Western Reserve University, USA, from April, 1988.

Researches in progress are as follows.

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

(2) Bipolar electrode cell developed for the aluminum electrowinning has been applied to obtain liquid magnesium from the chloride melt at 750°C.

(3) 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.

(4) 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.

(5) Corrosion and inhibition mechanisms of copper and copper alloys have been studied with organic inhibitors. Simulation tests have been conducted to reproduce a new mode of corrosion which has recently been observed in air-conditioning heat exchangers. The corrosion is characterized by complicated microscopic caverns with porous copper oxides connected by tunnels.
(6) A stacked rotating bipolar electrode cell is being tested for the electrochemical treatment of dilute cyanide solution containing heavy metal ions. The fundamental studies on recovery of gallium from Bayer solution are in progress.
(7) In order to elucidate the effect of small gas bubbles in tap water on the corrosion of pipe-line materials, loop-tests of corrosion are carried out under controlled conditions.

Oral Presentation

Behaviors of Various Elements in the Refining Process of Crude Aluminum Chloride; I. Oohira, S. Konda, T. Narita and T. Ishikawa: The 14th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1988.

On the Removal of Inhibitive Substance in Bayer's Liquor for Direct Electrodiposition of Gallium Metal; T. Sasaki and T. Toyoda, T. Ishikawa: *ibid.*

A New Mode of Corrosion in Heat Exchanger Copper Tubes in Humid Atmosphere with Alkyl Carboxylic Acid; T. Notoya and T. Ishikawa: The 23rd Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1988.

Studies on Energy Saving-High Performance Aluminum Production Technique by Electrolysis of High Temperature Molten Salts having Aluminum Chloride; T. Ishikawa, S. Konda and T. Narita: The 106th Annual Meeting YOYUEN, Feb., 1988.

Analysis of Hydrotalcite on Aluminum Brasses; T. Notoya: Corrosion Committee Meeting of Japan Copper Development Association, Mar., 1988.

Corrosion Potential and Polarization Characteristics; T. Ishikawa: The 55th Annual Meeting of Electrochem. Soc. of Japan, Apr., 1988.

Electrowinning of Magnesium by Using Stacked-Type Bipolar Electrode Cell; N. Yokoyama, S. Konda, T. Narita and T. Ishikawa: *ibid.*

Unusual Form of Corrosion in Copper Tubes; T. Notoya and T. Ishikawa: The 55th Spring Meeting of Japan Chemical Society, Apr., 1988.

Joining of Fully Stabilized Zirconia to Metals (Part 1) Application of Active Metal Filler and Ni-W Interlayer; T. Narita, T. Mitsueda and T. Ishikawa: The 102nd Spring Meeting of Japan Institute of Metals, April 1988.

Joining Mechanism of Silicon Nitride Ceramics and Stainless Steels; K. Miura, T. Narita and T. Ishikawa: *ibid.*, April 1988.

Joining of Alumina Ceramics and Metals Using Active Metal Filler and Ni-W Interlayer; T. Narita and T. Ishikawa: *ibid.*, April 1988.

Break-down Phenomena of Preformed Chromic Oxide Scales on Fe-25Cr Alloy in Hydrogen-Hydrogen Sulfide Gas Mixtures; H. Takahashi, T. Narita and T. Ishikawa: *ibid.*, April 1988.

High-Temperature Sulfidation of Austenitic Stainless Steels in H_2-H_2S Gas Mixtures; T. Narita and T. Ishikawa: 1988 MRS International Meeting on Advanced Materials, May 1988.

Bonding Layer Structures and Their Changes with Heat Treatment of Si_3N_4 and Fe-26Cr Bondings; K. Miura, T. Narita and T. Ishikawa: *ibid.*, May 1988.

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Joining of Silicon Nitride Ceramics to Metals with a Ni-Cu-Ti Filler; K. Miura, T. Narita and T. Ishikawa: *ibid.*, June, 1988.

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Fracture Strength of Si_3N_4/Metal Joinings at High Temperatures; K. Miura, T. Narita and T. Ishikawa: 103rd Fall Meeting of JIM, October, 1988.

Measurement of SAW Propagation Velocity of Partially Stabilized Zirconia Ceramics Joined to Metals; T. Narita, T. Ishikawa and I. Ishikawa: *ibid.*, October, 1988.

High-Temperature Corrosion of Pre-Oxidized Fe-Cr-Al-Y Alloys in H_2-H_2S Atmospheres; H. Takahashi, T. Narita and T. Ishikawa: *ibid.*, October, 1988.

Temperature Dependence of Fracture Strength of Ceramic/Metal

Joinings; K. Miura, T. Narita and T. Ishikawa: The Hokkaido Section Fall Meeting of JIM, November, 1988.

The Relationship between Current and Voltage Estimated on the Bipolar Electrode Cell for Electrowinning of Aluminum from Chloride Melts; T. Ishikawa, T. Narita and S. Konda: The 2nd China-Japan Bilateral Conference on Molten Salt Chemistry and Technology, Nov., 1988.

Inhibition of Dezincification of Brasses by Organic Inhibitors; T. Notoya: The 28th Meeting of Japan Copper and Brass Research Association, Nov., 1988.

White Scale Formed on Aluminum Brass in Sea Water and Its Role in Corrosion Prevention; T. Notoya, T. Tsuji, T. Nishijima, H. Kunieda, K. Nagata, T. Atsumi T. Minamoto and T. Kawashima: The Hokkaido Section Fall Meeting of JIM, Nov., 1988.

Corrosion of SUS 304 Stainless Steel in Oxalic Acid Solution

T. Morozumi, M. Moriya, K. Ogura
and Y. Takemoto

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 139, 49-54 (1988)

The corrosion rate of oxidized and unoxidized SUS304 stainless steel was measured in 0.1 M oxalix acid at 80°C under the potentiostatically polarized conditions.

The dissolved amounts of Fe, Cr and Ni were determined by atomic absorption analysis after 166 min of polarization as a function of the potential. The corrosion potential and the sweep potentiostatic polarization curve were also measured in the same solution.

The unoxidized specimen was severely attacked at the cathodic potential between -200 and -700 mV vs Ag-AgCl. Similar cathodic corrosion was also found, but with a decreased dissolution rate, for oxidized specimens. Since the corrosion potential of the alloy situated nearly at the boundary of active-passive transition, both specimens frequently suffered localized attack due to insuficient passivation during spontaneous immersion.

The dissolution rate of the surface oxide was slightly affected by the electrode potential within the active and passive regions. Therefore, weakly anodic polarization is desirable for the dual purposes of the effective dissolution of surface oxide and the protection of substrate alloy surface. (Japanese)

Study of Piezoelectric Response to the Active Dissolution/Passivation of Nickel in Weakly Acidic Sulfate Solution

Xiang Chun Jiang, Masahiro Seo and Norio Sato

Boshoku Gijutsu, **37**, 191 (1988)

The piezo-electric detection was applied to nickel electrode in 0.5 mol/dm^3 sulfate solutions (pH$=$3.0 and 5.8) to measure the potential of zero charge (PZC) and to investigate the active dissolution/passivation.

The PZC of nickel electrode in pH 3.0 sulfate solution directly measured from the piezoelectric signals was -0.15 V (SHE). The frequency analysis of piezo-electric response to the active dissolution/passivation was performed on basis of the proposed reaction mechanism to provide the separated two terms of q_M and Q; the former is a surface charge density of nickel electrode and the latter is an apparent charge density caused by adsorption. The total constant, k_a, involving dissolution and passivation processes, evaluated from the frequency analysis was about $6\times10^2\,s^{-1}$ and $3\times10^3\,s^{-1}$ for the solution of pH 3.0 and pH 5.8, respectively.

The value of Q was derived as a function of rate constant of elemental reaction step and coverage of intermediate adsorbates. The competitive processes of active dissolution and passivation was discussed from the potential dependence of Q. (Japanese)

Photoacoustic Study on Cathodic Reduction of Anodic Oxide Films Formed on Copper in Borate Solution

Masahiro Seo, Xiang Chun Jiang and Norio Sato

Werkstoffe und Korrosion, **39**, 583 (1988)

An in-situ photoacoustic (PAS) technique, using a piezoelectric detector with high sensitivity was applied to the study on duplex oxide films anodically formed on copper in pH 8.4 borate solution. The PAS signals from the copper electrode were produced by an irradiation of light beam with a wavelength of 514.5 nm.

The PAS amplitude during cathodic reduction of the outer oxide layer to Cu_2O changed in the opposite direction, depending on the anodic potential of film formation and oxidation time. Assuming that the change in PAS amplitude is proportional to both optical absorption coefficient and film thickness, it was deduced from comparison of the estimated absorption coefficients for $Cu(OH)_2$, CuO and $CuO_{0.67}$ films that dehydration of the outer layer having an average composition of $CuO_x(OH)_{2-2x}$ proceeded with increasing anodic potential of film formation and oxidation time during growth of the duplex oxide film.

Moreover, it was found that the change in PAS amplitude during cathodic reduction of the total Cu_2O film involving the inner layer to metallic copper was proportional to the electric charge required for cathodic reduction, i. e., the film thickness, irrespective of anodic potential of film formation and oxidation time, which proved the validity of the above assumption. (English)

Breakdown and Repair of Passive Films

Masahiro Seo

Memories Tech. Meeting Corr. Eng. Div., Soc. Mater.
Sci. Jpn., No. 144, Vol. 27, Part 3, 1 (1988)

The high corrosion resistance of stainless steel is sustained by a very thin oxide film, i. e., passive film. The composition, structure and functions of the passive film sensitively depend on the alloying elements in the steel and the environments in which the steel is used. The passive film is always locally broken and repaired repeatedly. The local breakdown of passive film is caused by not only the heterogeneity of the steel surface but also the fluctuation of electrode potential and electrolyte concentration. The various factors influencing on the local breakdown and repair of passive film were discussed in relation to the roles of alloying elements on the corrosion resistance of stainless steel. (Japanese)

Some Approaches for Understanding the Passive Film of Iron

Toshiaki Ohtsuka

Boshoku Gijutsu, **37**, 228 (1988)

Some theoretical approaches were reviewed for understanding the passive behaviour of iron electrode. On the thermodynamic approach the electrochemical equilibrium of chemical species was assumed at any interface, resulting in a potenital difference in the passive film which should be accompanied by a difference of chemical potentials. On the ionic conductor approach the high-field-assisted ion migration connected with the ionic charge transfer at the passive film/solution interface originates a potential difference in the film. The prediction from the approach for the thickness-potential relation dependent on solution pH is in agreement with the experimental result. On the semiconductive oxide electrode approach the electronic equilibrium plays an important role, which yields a depletion layer for free electric carrier in the film. The depletion layer functions as a dielectric layer which sustains a potential difference in the film. (Japanese)

Unusual Corrosion in Copper Tubes

T. Notoya, T. Hamamoto and K. Kawano

Boshoku Gijutsu **37**, (No. 2), 110 (1988)

Uniform oxidation is the most common type of corrosion of copper tubes in refrigerating and air-conditioning units. Recently an unusual type of corrosion, "Formicary corrosion", has been reported in such copper tubes during leakage tests after manufacture or after short periods of use. The corrosion is characterized by complicated microscopic caverns of porous copper oxide connected by tunnels. The microcaverns have voids and microcracks and the surface of the copper tubes is tarnished greyish-brown or blue-violet with bulky corrosion products and shows no obvious defects indicating the leaks. Twenty one cases of such premature failures of copper tubes discovered during the four years from 1984 to 1987 are shown in Table 1. In a few cases carboxylic acids may have been the corrosive media, because formic and acetic acids were detected in the atomosphere where the copper tubes were placed.

Experiments produced similar corrosion after copper tubes were exposed to a humid oxygen atmosphere with small amounts of carboxylic acids for a few months. The carboxylic acids were formic acid, acetic acid, propionic acid, and n-butyric acid. The mechanisms of propagation of the corrosion and preventive measures are presented. (Japanese)

Pitting Propensity Tests for Copper Tubes in Supply Waters by Using BNF Electrochemical Cell

T. Notoya

J. Japan Copper and Brass Research Association
Vol. 27, 147 (1988)

Evaluation of pitting corrosion propensity of supply waters was made by use of the BNF electrochemical cell which has been developed by British Non-Ferrous Metals Technology Centre to determine a water capability to support Type I pitting of copper tubes. Twenty different waters tested included tap waters, natural well waters and artificial waters having different composition. The cell assembly, method of operation and interpretation of the results are described. The prevalent types of pitting attack in copper tubes are classified. Merites and shortcomings of the BNF cell were pointed out. Feasibility of the BNF cell application was examined to Type II pitting attack which is the most prevalent type of pitting attack in Japan. It is concluded that the BNF cell showed well the pitting propensity of waters susceptible to Type I pitting but is not sensitive for those to Type II pitting. It is suggested that morphology and coverage of corrosion products formed on the center and surrounding anode elements in the BNF cell determine the water aggressiveness to copper tubes. (Japanese)

Corrosion Inhibition of Copper Alloys in Ball-Point Pen Vehicles

Takenori Notoya

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 142 p. 1 (1988)

Corrosion products prevent a continuous flow of ink by clogging within ink-flowing paths in copper alloy ball-point pen tips, particularly after a long time of non-use under adverse conditions. Microscopic observation of the ink-path surfaces were roughened by heterogeneous dissolution, deposition of insoluble corrosion products, and a number of microcracks perpendicular to the drilling direction in oxide stripped substrates. In order to improve the performance and extend the service life of ball-point pens by preventing the formation of the ink-blocking corrosion products, screening tests of suitable organic inhibitors such as ink additives were conducted to mitigate corrosion of three copper alloys as the tip materials in a simulated solvent in the presence of inhibitors. Effectiveness of the inhibitors were evaluated by visual observation of the immersed surfaces of nickel silver, 60/40 brass and bronze and 30 day weight loss measurements in a mixture of benzyl alcohol (4 parts by volume) and oleic acid (1 part) containing inhibitors under stagnant conditions at 60°C.

The inhibitors tested were benzotriazole and three benzotriazole derivatives, two benzimidazoles, mercaptobenzothiazole, phenyl thiourea, dimercaptothiadiazole and dimethyldithiocarbamic acid.

It was found that benzotriazole, together with its methyl-and carboxylic derivatives, and dimercaptothiadiazole were effective for the copper alloys in preventing dissolution and formation of clogging masses of the metallic soap in the solvents. (Japanese)

Potentiostatic Dezincification of Commercial Brasses and Its Inhibition by Organic Inhibitors in Acidified Sodium Chloride Solution

Takenori Notoya

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 144 p. 7 (1988)

Inhibition action of three organic chemicals as dezincification inhibitors for six different commercial brasses was investigated using a potentiostatic acceleration technique in an acidified 0.5 M NaCl solution at 60°C. Brasses used were two dezincification resistant brasses of TCA (0% β phase) and NFS (9%), C2604 (14%) free cutting brass, C4641 (22%) naval brass, C3771 (27%) forging brass and C6782 (62%) high strength brass. Inhibitor performance was in the order of tolyltriazole (TTA) $<$ benzotriazole (BTA) $<$ thiabendazole (TBZ) based on chemical analysis for dissolved copper and zinc during anodic polarization at -0.200 V vs. S. C. E. It was concluded that dezincification attack in the brasses can be prevented by an addition of a small amount (1 mili mol.) of either TTA, BTA or TBZ to dezincification prone environments. (Japanese)

Effect of pH on the Distribution of Anions in Anodic Oxide Films Formed on Aluminum in Phosphate Solutions

H. Takahashi, K. Fujimoto and M. Nagayama

J. Electrochem. Soc., **135**, 1349-1353 (1988)

The composition of anodic oxide films anodically formed on aluminum in phosphate solutions with different pH's was examined by chemical sectioning in a sulfuric acid solution combined with impedance measurements, solution analysis, and electron microscopy The oxide films were found to consist of two layers: an outer layer containing phosphate and an inner layer consisting of pure Al_2O_3. With increasing pH of the anodizing solution, the thickness of the outer layer increases and the phosphate concentration in the outer layer decreases. In the chemical sectioning, the dissolution rate of the outer layer increases with anodizing solution pH, while the dissolution rate of the inner layer is slower and unaffected by the anodizing solution pH. For the outer layer, there is a linear relationship between the phosphate concentration and the sectioning rate in the sulfuric acid solution. The mechanism of film formation during anodizing is discussed in terms of Al^{3+} transport through the oxide. (English)

Effect of Heat Treatment of Hydroxide on the Formation of Composite Oxide Films on Aluminum

H. Takahashi, M. Yamagami, R. Furuichi
and M. Nagayama

Proc. Symp. on Electrochem. Technology in Electronics,
(Edited by L. T. Romankiw & T. Osaka,
Electrochem. Soc.) p. 287～300 (1988)

Aluminum specimens covered with hydroxide Films were heat-treated at $T_{age} = 25°C - 500°C$ to examine the structural change in the hydroxide film with T_{age} by FTIR, gravimetry, and electron microscopy. The heat-treated specimens were anodized in a neutral borate solution at 80°C with a constant c. d. to form the "composite oxide films", and the anodizing behavior was followed by measuring the anode potential, and the amount of dissolved Al^{3+} ions as well as by electron microscopy.

It was found that with heat treatment at $T_{age} \leq 300°C$ hydroxide films consisting of pseudo-boehmite ($Al_2O_3 \cdot 2.5H_2O$) release water to form boehmite ($Al_2O_3 \cdot H_2O$), and that beyond this temperature boehmite changes to anhydrous alumina (Al_2O_3).

For specimens heat-treated at $T_{age} \leq 300°C$ heat treatment was observed to facilitate the formation of composite oxide films. For specimens heat-treated at $T_{age} \geq 300°C$, however, local dissolution of the metal substrate and gas evolution were observed during anodization.

The formation mechanism of composite oxide films is discussed in relation to the structural change in the hydroxide with heat treatment. (English)

Depth-profiling of Metal Oxide Films Prepared with MOCVD

Masahiro Seo, Katsuya Takemasa and Norio Sato

Applied Surface Science, **33/34**, 120 (1988)

Metal oxide films (Cr_2O_3 and Fe_2O_3) were prepared on platinum substrate by metal organic chemical vapor deposition (MOCVD). Depth-composition profiles of the metal oxide films were measured by the simultaneous use of Auger electron spectroscopy and argon-ion sputtering. The composition broadening, ΔZ, at the film/substrate interface was evaluated as a function of film thickness, Z, from the measured depth profiles. The relative depth resolution defined by $\Delta Z/Z$ improved rapidly with film growth and then maintained a constant value, which was about one third as much as that of the Cr_2O_3/Cr or Fe_2O_3/Fe system prepared with dry oxidation. The predominant factors (surface roughness and film structure) influencing the relative depth resolution have been discussed. (English)

Structure and Property of Oxide Films Formed on Aluminum

Hideaki Takahashi

J. Surf. Scie. Soc. Jpn., **9**, 720-725 (1988)

Structures of typical oxide films formed on aluminum, and the structural changes with a combination of treatments are reviewed.

Oxide films on Al are classified into four typical groups by structure: porous oxide films, barrier oxide films, thermal oxide films, and hydroxide films. The porous oxide films are formed anodically in acid solutions and barrier oxide films in neutral solution and the thermal oxide films are formed by heat treatments and hydroxide film by hydrothermal treatments. The morphology and formation behavior of these oxide films are described briefly.

Three characteristic phenomena observed with the combination of treatments are described: porefilling, sealing, and formation of composite oxide films. Pore-filling, where pores of porous oxide films are filled with new oxides, takes place by anodizing porous oxide-covered Al in a neutral solution, and is useful for determining the porosity of the oxide film. Sealing of pores in oxide films is attained by hydration of oxide exposed to hot water, and the dissolution rate of the sealed oxide film is much lower than that of unsealed film. Composite oxide films are formed by anodizing hydroxide-covered Al in neutral solutions, and the growth of the oxide film proceeds by dehydration of hydroxide at the hydroxide/oxide interphase and formation of oxide at the oxide/metal interphase. (Japanese)

Electrochemical Formation of Zr(IV)-Cr(III) or Ti(IV)-Cr(III) Composite Oxide Films on Stainless Steel

Hidetaka Konno and Ryusaburo Furuichi

J. Metal Finish. Soc. Japan, **39**, 29 (1988)

It was found that Zr(IV)-Cr(III) or Ti(IV)-Cr(III) composite oxide film is formed on a stainless steel by cathodic polarization in a chromate solution containing Zr(IV) or Ti(IV) ions. The method provided good oxidation resistance to SUS430 stainless steel at elevated temperatures. In principle, it is possible to develop other composite oxide including Y(III), Ce(IV), La(III), Gd(III), and others. The present method is similar to commonly used electrolytic chromate treatment, and it has potential advantages for practical applications. (Japanese)

In-Situ Raman Spectroscopy of Manganese Dioxide During the Discharge Process

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

J. Electroanal. Chem., **243**, 219 (1988)

The discharge reduction process of an electrodeposited MnO_2 layer was measured by Raman spectroscopy under in-situ condition with MnO_2/Au electrodes. The Raman spectrum of the MnO_2 layer on Au changes with potential in a reversible manner. From 0.80 V to 0.20 V there are almost no changes in the Raman spectrum, although a small amount of cathodic current of a few μA flows on the voltammogram. The small amount of the cathodic charge in this potential region may not introduce any important change in the MnO_2 lattice.

At potential more negative than 0.20 V the Raman peak disappears. It may therefore be suggested that the reduction in this potential exceeds a critical point for the transformation of the $MnO_2+MnOOH$ single later, beyond which the reduction product cannot maintain the same lattice structure as that of the oxidized form of MnO_2. (English)

The Surface Scanning Photoelectrochemical Imaging

Kazuhisa Azumi

BOSHOKU GIJUTSU, **37**, 379-380 (1988)

Photoelectrochemical imaging (photoelectrochemical microscope) technique using surface scanning photocurrent is reviewed. This technique has been developed for the investigation of surface observation of metal and semiconductor electrodes on which defects, localized corrosion and degradation, and surface decoration is detected as the photo-induced current in a electrochemical cell. The spot light from a laser source is two-dimentionally scanned on the electrode surface, and photocurrent is recorded as a function of the position on the surface, resulting in an image of localized photoelectrochemical property. The investigations on titanium, galiumphosphate, tungusten diselenide and ruthenium modified selenide are introduced. (Japanese)

On the Specific Conductivity and Decomposition Voltage of Chloride Melts Containing $AlCl_3$

Shoichi Konda, Toshio Narita and Tatsuo Ishikawa

Bulletin of the Faculty of Engineering,
Hokkaido University, **143**, 135 (1988)

This report includes the specific conductivity and decomposition voltage of $AlCl_3$ in a NaCl-25 mol% $MgCl_2$ melt, determined by the coexistence of aluminum particle products and chlorine gas bubbles during electrolysis at 750°C.

By increasing $AlCl_3$ contents from 2 to 9 mol% $AlCl_3$, the specific conductivity decreased from 2.30 to 1.85 S/cm and the decomposition voltage from 2.005 to 1.985 V. When the resistivities were obtained from the I-V curves and plotted against the electrode distance, at zero electrode distance they were in the range 0.008 to 0.022 ohm, not zero. This resistivity seems to be due to nuclei producing chlorine gas bubbles on graphite electrode.

With these parameters the relations between current and voltage were discussed for electrowinning of aluminum from the chloride melt containing $AlCl_3$, and the cell efficiency and the minimum energy consumption could be determined for different sizes of bipolar electrode cell. (Japanese)

Studies on Energy Saving-High Performance Aluminum Production Technique by Electrolysis of High Temperature Molten Salts having Aluminum Chloride

Tatsuo Ishikawa, Shoichi Konda and Toshio Narita

YOYUEN **31**, 61-76 (1988)

In this paper, firstly, experimental studies on the electrowinning of liquid aluminum from chloride melts having aluminum chloride were summerized. In order to develop an energy-saving and high-productive process, these studies have being carried out in our laboratry during more than ten years.

Thermal conductivity measuring procedures were also described for a tube-stacked wall, which structure was devised to minimize the melt permeation into bipolar electrode cell wall for industrial application.

Then, a self-heating simulated cell with the tube-stacked wall was constructed of five reaction zones and an electrowinning operation of this cell was carried in the chloride melt under an applied current of 260 ampere. (Japanese)

The Relationship between Current and Voltage Estimated on the Bipolar Electrode Cell for Electrowinning of Aluminum from Chloride Melts

Tatsuo Ishikawa, Toshio Narita and Shoichi Konda

Proceedings of the Second Japan-China Bilateral
Conference on Molten Salt Chemistry
and Technology, 63 (1988)

In order to develop a bipolar electrode cell suitable for electrowinning of liquid aluminum and its alloy from the chloride melts, an estimating procedure for bath voltage and cell efficiency at various applied currents was proposed using an equivalent circuit of the bipolar electrode cell.

The validity of this estimation was confirmed experimentally by operating the laboratory-scale cells, about which had been known the following data ; number of the bipolar electrodes, total sectional area of the cell, average sectional area and thickness of the electrodes, electrode spacing, specific conductivity and decomposition voltage of the melt at various concentrations of aluminum chloride at operational temperature. (English)

Breakaway of Type 430 Stainless Steel in Water Vapor/Oxygen Atmospheres at Elevated Temperatures

Hidetaka Konno, Isao Saeki and Ryusaburou Furuichi

Boshoku Gijutsu **37**, 228–345 (1988)

The oxidation behaviour of type 430 stainless steel was studied in a range of 1223 to 1373 K, in a gas mixture of H_2O ($P_{H_2O}=0.006\sim0.20$ atm), O_2 ($P_{O_2}=0.165$ atm), and N_2 ($P_{N_2}=$balance) under atmospheric pressure. Breakaway due to water vapor was found to take place in a manner of localized corrosion. It was also found that the lifetime to breakaway, t_L, is not simply determined by the oxidation conditions, but can be evaluated statistically. An exponential distribution explains the scattering of t_L data. Both the transition probability of breakaway, λ, and the apparent parabolic oxidation rate constant before breakaway, k_p'', increases with an increase in P_{H_2O}, indicating that larger k_p'' in the initial stage leads to earlier breakaway. As the mass gain by oxidation at the breakaway point did not change very much with P_{H_2O}, the accumulation of growth stress in the oxide film will be one of the controlling factors of film breakdown leading to breakaway. The crystalline structure and the surface composition of the oxide film did not change very much with P_{H_2O} before breakaway, suggesting that orther structural differences, such as defect concentration, ionic conductivity, or others, can explain the effect of water vapor. (Japanese)

High Temperature Behavior of the Zinc Vapor Diffusion-Coated Layer on Copper Surface

Tsuyoshi Yamamoto, Toshio Narita
and Keizo Nishida

J. of Japanese Surface Finishing
39 (No. 1), 1988, 1-5

Copper test pieces were diffusion-annealed in an evacuated capsule at 1073 K for 3.6 ks with chips of a Cu–Zn alloy as a zinc vapor source. The test pieces were homogenizing-annealed or oxidized at 1073 K for 1.8∼60.3 ks.

Variations in the observed surface concentration of zinc with homogenizing-annealing time differed from those calculated by the equation reported by Whittle, but coincided approximately with those calculated using an equation taking into account the concentration-dependence of interdiffusion coefficients.

In the oxidation experiments, sudden increases in oxide layer thickness were found after a certain oxidation time. A definite difference was found between observed values for the variations in surface concentration of zinc with oxidation time and the theoretical values obtained by Whittle. (Japanese)

The Metallization on a Si_3N_4 Ceramics by Using Cr Vapor

Toshiyuki Takashima, Tsuyoshi Yamamoto
and Toshio Narita

J. of Japanese Ceramic Society,
96 (No. 1), 1988, 1-5

Formation of Cr-metallized layer on the surface of Si_3N_4 ceramic by the vapor-diffusion method was studied. The metallization was carried out in a quartz capsule at 1273 K for up to 72 ks. As a vapor source, pure Cr powder was used. The kinetics of layer growth was parabolic with the rate constant of $1.0 \times 10^{-14} m^2 \cdot s^{-1}$ at 1273 K. The metallized layer was composed of two lyers; Cr_2N and CrN at the surface layer and Cr_2Si at the inner layer as identified by the X-ray diffraction analysis. The hardness of the metallized layer increased gradually from H_v 668 at surface to H_v 1179 at inner part. (Japanese)

Pulverization Process and Its Prevention by Copper Plating of Fe-Ti Hydrogen Storage Alloy

T. Mizuno, J. Kitabuki, Y. Hayashi
and T. Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 141, 193-200 (1988)

Pulverization of Fe-Ti hydrogen storage alloys was studied by using an acoustic emission method, as well as the BET surface area measurement including scanning electron microscopic observation.

The acoustic emission occurred remarkably in the first cycle of hydrogen absorption into virgin alloy, but practically disappeared during and after the second cycle of hydrogen absorption and desorption. The SEM image indicated the occurance and the growth of micro fissure network that was almost completed all over the alloy grains during the first cycles of hydrogen absorption in correspondence with the increase in the BET surface areas. The electroless copper plating was effective for preventing the pulverization when it was applied for the alloy which had already absorbed hydrogen, but was not effective for virgin alloy. The necessary thickness of copper plating layer was determined to be about 0.2% of mean alloy particle diameter.

This technic seems to be advantageous since it is low cost and does not markedly affect the hydrogen storage performances.
(Japanese)

Ylide-Metal Complexes. XIV. An X-Ray Photoelectron Spectroscopic Study on Tellurium Complexes of Methylenetriphenylphosphorane

Hidetaka Konno and Yoshihisa Yamamoto

Bull. Chem. Soc. Jpn., **61**, 2990-2992 (1988)

A series of new tellurium complexes of methylenetriphenylphosphorane, $(C_6H_5)_3P=CH_2$ (**L**), namely, dichlorobis(methylenetriphenylphosphorate)tellurium dichloride, $[L_2TeCl_2]Cl_2$, chlorotris(methylenetriphenylphosphorane)tellurium trichloride, $[L_3TeCl]Cl_3$, and tetrakis(methylenetriphenylphosphorane)tellurium tetrachloride, $[L_4Te]Cl_4$, were examined by XPS. Binding energies of Te 3d electrons for the complexes are considerably lower than those for common Te(IV) compounds such as $(C_6H_5)_2TeCl_2$, $TeCl_4$ (correctly Te_4Cl_{16}) and others, and they diminished with increasing number of **L**'s and decreasing number of bonded chlorine atoms, indicating that **L** is an electron donor. Bonded chlorine atoms and free chloride ions were clearly distinguished from the binding energy of Cl $2p_{3/2}$ electrons. (English)

Determination of the Stability Constants of Zn^{2+}-MnO_2 Surface Complexes

Hiroki Tamura, Noriaki Katayama
and Ryusaburo Furuichi

Bunseki Kagaku, **37**, 395-399 (1988)

The adsorption isotherm for Zn^{2+} ions on MnO_2 was analyzed by considering the formation of Zn^{2+}-MnO_2 surface complexes, and the stability constants of the surface complexes were determined. The surface of MnO_2 in water is covered with acid and base hydroxyl groups. The acid group, $\equiv MnOH(a)$, was assumed to be the site of the complexation, and the reactions were expresed by

$$Zn^{2+} + NO_3^- + \equiv MnOH(a) \rightleftharpoons \equiv MnOZn^+ \cdot NO_3^- + H^+ \qquad (1)$$

$$Zn^{2+} + 2\equiv MnOH(a) \rightleftharpoons (\equiv MnO)_2Zn + 2H^+ \qquad (2)$$

The stability constants of the formed (1 : 1) and (1 : 2) surface complexes, K_1 and β_2, were derived as

$$K_1 = \frac{[\equiv MnOZn^+ \cdot NO_3^-][H^+]}{[Zn^{2+}][NO_3^-][\equiv MnOH(a)]} \times \exp(B_1[\equiv MnOZn^+ \cdot NO_3^-]) \qquad (3)$$

$$\beta_2 = \frac{[\equiv (MnO)_2Zn][H^+]^2}{[Zn^{2+}][\equiv MnOH(a)]^2} \exp(B_2[(\equiv MnO)_2Zn]) \qquad (4)$$

where the exponential terms contain the concentration of the surface complexes (mol m^{-2}) and constant B_1 and B_2 (m^2 mol^{-1}); the exponential terms express the retardation of further complexation by the complexes already formed. The equations (3) and (4) together with the mass balance equation for the adsorption site were fitted to the adsorption isotherm, and the values of the constants were determined by the nonlinear least squares method. The values are: $K_1 = 1.22 \times 10^{-4}$ m^3 mol^{-1}, $\beta_2 = 6.86 \times 10$ m^{-1}, $B_1 = 1.51 \times 10^6$ m^2 mol^{-1}, and $B_2 = 28.8 \times 10^4$ m^2 mol^{-1} at $[NaNO_3] = 0.1$ mol dm^{-3} and 25°C. The fit between the constants and the isotherm was excellent. (Japanese)

Adsorption of Zn(II) Ions on MnO_2 in NH_4Cl Solutions

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Progress in Batteries & Solar Cells, **7**, 44-48 (1988)

The adsorption behavior of Zn(II) ions on MnO_2 in NH_4Cl solutions was examined as a function of pH and the concentrations of Zn(II) and NH_4Cl. The amount of adsorbed Zn(II) increased with increasing pH and Zn(II) concentration, while it decreased with increasing NH_4Cl concentration. The most predominant Zn(II) species in $1 \sim 4$ mol/dm^3 NH_4Cl solutions with pHs less than 7 was calculated to be a Zn(II) trichloro complex, $ZnCl_3^-$, and the predominant surface species on MnO_2 were estimated to be undissociated acid and base hydroxyl qroups, $\equiv$MnOH(a) and $\equiv$MnOH(b). The adsorption was considered to occur through the following reaction :

$$ZnCl_3^- + \equiv MnOH(a) \rightleftharpoons \equiv MnOZn^+ \cdot Cl^- + H^+ + 2Cl^-$$

This reaction quantitatively explained the effect of pH and the concentrations of Zn(II) and NH_4Cl on the adsorption of Zn(II). (English)

DTA Study on α-Fe_2O_3 Formation From Fe(III)-Hydroxides Containing Foreign Metallic Ions

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Thermochimica Acta, **133**, 101-106 (1988)

The formation of α-Fe_2O_3 from Fe(III)-hydroxides containing the different metallic ions (Me) was studied with DTA, TG and XRD; Me^{2+}'s were Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} and Me^{3+}'s were Al^{3+} and Cr^{3+}. The mixing of Me was carried out by three procedures: co-precipitation, gel-mixing and mortar-mixing. Sample-F of Fe(III)-hydroxide containing no Me was prepared from $Fe(NO_3)_3$ and NaOH solutions at pH=12. The sample showed an endothermic DTA peak at Td=100°C due to the dehydration and an exothermic peak at Tc=414°C corresponding to the formation of α-Fe_2O_3. The co-precipitation samples containing 10 mol% of Me showed Tc=527°C for Cu^{2+}, 528°C for Co^{2+}, 550°C for Zn^{2+}, 554°C for Mg^{2+}, 559°C for Ni^{2+}, 473°C for Al^{3+}, and 480°C for Cr^{3+}. The Tc value increased with an increase in the amount of Me mixed between 0 and 10 mol%. The different mixing procedures for 10 mol% of Cu^{2+} were observed to give Tc=527°C for co-precipitation, 517°C for gel-mixing, and 414 and 494°C for mortar-mixing. These results suggest that (1): the foreign Me's forming ferrite retard the formation of α-Fe_2O_3 more than Me's forming solid solution with α-Fe_2O_3 and (2): the mixing procedure affects the degree of incorporation of Me in the Fe(III)-hydroxide. (English)

Determination of the Dissociation Constants of Surface Hydroxyl Groups

—Application to the Characterization of Metal Oxides—

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Bulletin of the Japan Institute of Metals,
27, 158-164 (1988)

Metal oxides in aqueous solution act as acids and bases to adsorb ions. This property is due to the surface hydroxyl groups formed by dissociative chemisorption of water molecules on the oxide. The hydroxyl groups exhibit different acid-base properties for different oxides, and a quantitative description of the nature is important for characterizing metal oxides for various industrial applications. Several methods to determine the amounts of surface hydroxyl groups and the reported values for Al_2O_3, Fe_2O_3, MnO_2, SiO_2, TiO_2, and ZnO are described. Acid-base dissociation of surface hydroxyl groups forms charged sites on the oxides. The surface charge density, σ, can be measured by titration. The theoretical basis of the method is explained from the stoichiometry of the reaction. A method is proposed to determine the equilibrium constants for acid-base dissociation, in which the effect of σ on the dissociation is considered thermodynamically. The method is applied to MnO_2 samples for battery use. The values of the constants well explain the measured σ-pH relationships. (Japanese)

Structural Analysis of Hydrothermally Synthesized Nickel Ferrite

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Bulletin of the Faculty of Engineering, Hokkaido
University, No. 141, 183-191 (1988)

Nickel ferrite was prepared by hydrothermal treatment of hydrolysis products of mixture of nickel chloride and ferric chloride solutions, and characterized by X-ray diffraction, SEM observation, and Mössbauer spectroscopy.

The samples, treated at 75°C for 96 hours, showed only a weak indication of a peak at the strongest position in the X-ray diffraction pattern of nickel ferrite. X-ray diffraction patterns showed nickel ferrite formation above 100°C.

Formation and growth of nickel ferrite particles was virtually complete within 24 hours at temperatures between 100 and 250°C. The average particle size was from 15 to 35 μm with a maximum from 100 to 200 μm. Below 150°C the particles were angular, after 72 h at 200°C they were spherical, and after preparation for prolonged duration at higher temperatures they were platelike, due to cleavage. Since the patterns were quite similar to those of magnetite, nickel ferrite could not clearly identified by X-ray diffraction. Mössbauer spectroscopy, however, gave clear evidence of nickel ferrite at all temperatures above 100°C. This suggests the possibility of nickel ferrite formation through corrosion of Ni-containing steels in the environment of water coolant circuits of nuclear reactors. (Japanese)

Physicochemical Study of Crud Characterization Effect of Preparation Conditions on Magnetite Properties

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Bulletin of the Faculty of Engineering, Hokkaido
University, No. 139, 39-48 (1988)

About thirty specimens of magnetite were prepared by five methods under various conditions, and characterized X-ray diffraction, BET surface area measurement, Mössbauer spectroscopy, and SEM observation. The dissolution rate was also determined in three kinds of decontamination reagents: oxalic acid, EDTA, and EDTA-N_2H_4 solutions.

The morphologies of the products were divided into four groups: sphere, cube, octahedron, and fine particles. Although all of the specimens showed Mössbauer absorption spectrum composed of nine peaks which is typical to magnetite, the intensity ratio of the peak 2 to peak 1, I_2/I_1, varied with the preparation methods and conditions. The values of the I_2/I_1 ratio were distributed between 0.5 and 1.9, increasing with the decreasing BET surface area. The BET surface area was estimated to be 4 m^2g^{-1} when extrapolated to the limiting I_2/I_1 ratio, 2. The dissolution rate depends upon both the BET surface area and I_2/I_1 ratio. These findings suggest that the valence state of iron as well as the surface area plays important role in the dissolution of magnetite in the decontamination reagents. (Japanese)

The Role of Fins for the Diffusion Limiting Current in a Stacked Rotating Bipolar Electrode Cell

Takeshi Sasaki and Tatsuo Ishikawa

DENKI KAGAKU, **56**, No. 1, 251 (1988)

The role of fins for mass transfer in a stacked rotating bipolar electrode cell was investigated by measuring the diffusion limiting current under variety of heights and number of fins with 0.01 M ferri/ferrocyanide in a 1 M NaOH aqueous solution ($M = mol \cdot dm^{-3}$). The distribution of the diffusion limiting current on the electrode surface was also determined using ring electrode. The rotation of the fins attached to the electrodes flattens the distribution of the limiting current across the electrode surface and simultaneously elevates the mass transfer rate. The distance of 1 mm from the top of fins to the opposite surface is small enough to raise the effective agitation to the opposite surface. The limiting current is little affected by the variation in the height and the number of fins. (English)