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CORROSION RESEARCH

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HOKKAIDO UNIVERSITY

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Visiting Professors

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and Prof. Dr. B. Lopez de Mishima

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Students

X. C. Jiang, K. Takemasa, H. Bogaki,
K. Aotsuka and A. Yamakawa

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

Semiconductive Properties of Passive Oxide Films

Characterization of the passive films on iron, titanium and zinc has been made as a semiconductor film on the metal surface. From the impedance measurements, the thickness of space charge layer in such semicoductive oxide films of n-type was determined which depends on the donor density and the dielectric constant of the oxides. The decay of photo-current suggestes that a significant density of the surface state exists on the oxide surface.

Theoretical Approch to Corrosion Resistivity of Alloys

A model was proposed in which the corrosion resistivity of alloy was closely related to the selective dissolution and surface enrichment of alloying elements. It is assumed that passivation

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begins to occur when the surface concentration of corrosion resistant alloying elements exceeds a critical level.

The kinetics of surface enrichment was derived by taking into account the selective dissolution rate at the alloy surface and the interdiffusion rate in the alloy substrate.

Surface Characterization of Metal Oxide Films

Metal oxide films (Cr_2O_3 and Fe_2O_3) and their multilayer films were prepared on platinum substrate with a metal organic chemical vapor deposition (MOCVD). The depth-profiling of MOCVD films was performed with simultaneous use of Auger electron spectroscopy and argon-ion sputter-etching technique with relation to a new research on the corrosion resistance and photo-electrochemical behavior of MOCVD films.

The depth-composition profiles of the passive films formed on Fe–26Cr alloy in a high-temperature ($150°C \sim 250°C$)-boric borate solution were also measured to investigate the formation process of the passive film in high-temperature-high pressure-aqueous solutions. From the depth-composition profiles, it was found that an inner oxidation took place in the film/substrate interface by inward-diffusion of oxygen ions through the outer oxide layer

Piezo-electric Response to Metal Electrodes

The frequency analysis of piezo-electric signals for gold electrodes in alkaline sulfate solutions has unveiled molecular information on the electrosorption of OH^- ions and the subsequent process of monolayer oxide formation. The piezo-electric signals of passive copper and nickel electrodes were measured to evaluate the contribution of the space charge in the passive film to the surface stress. Furthermore, the measurement of photo-acoustic signals from gold and iron electrodes was initiated from this year in parallel with the peizo-electric detection.

Laser Raman Spectroscopy for the Electrochemistry

The laser Raman spectroscopy possesses an availability for composition estimation of the corrosion products of various metals under the in-situ condition in air or aqueous solution. The standard

spectra were measured of oxides and hydroxides of various metals such as iron, nickel, chromium, copper, etc.

Another application was performed to a manganese dioxide anodically deposited on a gold electrode. The Raman spectra of the thin deposition layer of manganese dioxide were measured as a function of the amount of the cathodic charge applied. The results suggest that the manganese dioxide changes to a disordered structure during the cathodic discharge process of battery.

Inorganic Membrane for the Proton Transfer

Tungsten oxyhydroxide is one of the conductors for both proton and electron. A membrane including the tungsten oxyhydroxide was used as a proton transducer and its proton conductivity was controlled as a function of the membrane electrode potential. A small change of the proton conductivity was observed in a potential region more negative than 0.5 V vs RHE, where the tungsten ion in the oxyhydroxide is reduced from the state of six valency to the state of five valency.

Other Activities

In 1986, Professor Seo attended the Corrosion Symposium at the 191st National Meeting of the American Chem, Soc. held in New York on April 13-19 and presented a paper entitled "A Theoretical Approach to Corrosion Resistivity of Alloys". Dr. Ohtsuka attended the 37th Meeting of the International Society of Electrochemistry held at Vilnius, USSR in August 24-31, 1986 and the International Conference on Structure and Dynamics of Solid/ Electrolyte Interfaces held at Berlin (West), September 2-5, 1986, to present two papers on the measurements of the anodic oxide films on Ti and W by using Raman and Infrared spectroscopies. Dr. Ohtsuka afterwards visited at the laboratories of Professor K. E. Heusler, Clausthal-Zellerfeld/W. Germany and of Professor J. S. L. Leach, Nottingham/G. Britain to discuss the anodic oxidation and passivation of metals.

The following scientists from over the sea paid the short visit to this laboratory in the year of 1986 : Dr. Hultquist from the

division of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden on Jan 6–13, 1986 and on July 28–August 4, 1986; Professor C. C. Nan from the Institute of Corrosion and Protection of Metals, Shenyang, China on April 25–May 6, 1986.

Prof. E. Chagas from the Institute of Chemistry, University of St. Paulo, Brazil, who was supported by the Japan International Coorperation Agency, stayed from July 21 to Oct. 15, 1986 to conduct the research on the surface treatment of superconducting alloys. Prof. H. T. Mishima and Prof. B. Lopez de Mishima from the University of Santiago Del Estero, Argentina, have joined this laboratory on Nov. 30, 1986 to make a collaborative work on the anodic oxides on metals.

Oral Presentation

Piezo-electric Response for the Surface Stress of Gold Electrode and its pH Dependence; X. C. Jiang, M. Seo and N. Sato: The 12th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1986

Analysis of Iron Passivation Films as a Semicondoctor—Mott-Schottky Plot; K. Azumi, T. Ohtsuka and N. Sato: The 21st Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1986

Assignment of Corrosion Products from Metallic Iron by using Laser Raman Spectroscopy; T. Ohtsuka, H. Ozawa, K. Kubo and N. Sato: *ibid*, 1986

Corrosion Resistivity and Surface Composition of Ferritic Stainless Steel Containing Copper; J. Guo, M. Seo and N. Sato: *ibid.*, 1986

On Composition broadening of the Oxide Film/Substrate Metal Interface due to the Argon Ion Sputter Etching; K. Take-masa, M. Seo and N. Sato: The 1986 Winter Meeting of the Hokkaido Section of the Japan Soc. for Analytical Chem. and Japan Chem. Soc., Feb., 1986

Surface Enrichement and Corrosion Resistivity of Alloys; M. Seo: The 2nd Meeting for the special division on corrosion of

electronic devices of Japan Soc. of Corrosion Engineering, Feb., 1986

Piezo-electric Response to the Stress Change of Iron Passive Films; M. Seo, X. C. Jiang and N. Sato: The 98th Spring Meeting of JIM, April, 1986

Measurements of Surface Stress Change of Metallic Electrode by Use of Piezo-electroc Response; M. Seo, X. C. Jiang and N. Sato: The 53rd Meeting of Electrochem. Soc. Japan, April, 1986

Film Growth of Tungsten Anodic Oxide Film and Its Electrochromism by Using Ellipsometry and Raman Spectroscopy; N. Goto, T. Ohtsuka and N. Sato: *ibid.*, 1986

A Theoretical Approach to Corrosion Resistivity of Alloys; M. Seo and N. Sato: Corrosion Symposium at the 191st National Meeting of the Am. Chem. Soc., New York, USA, April, 1986

Quantitative Analysis of Depth-Composition Profiles of Surface Oxide Films on Steel; M. Seo: Symposium on Surface Analysis and Surface Property of Japan Steel Association, June, 1986

Information on the Metal/Aqueous Solution Interface from Piezo-electric Response due to the Surface Stress Change; M. Seo, X. C. Jiang and N. Sato: '86 Spring Meeting of the Japan Soc. of Corrosion Enginerring, May, 1986

The Influence of Cu– and Nb–addition on Electrochemical Behavior and Surface Composition of Ferritic Stainless Steel; J. Guo, M. Seo and N. Sato: *ibid.*, 1986

Identification of Various Iron Rusts by Using Laser Raman Spectroscopy; T. Ohtsuka, K. Ozawa, K. Kubo and N. Sato: *ibid*, 1986

Kinetics of Selective Dissolution and Surface Enrichment of Alloys; M. Seo and N. Sato: The 1986 Summer Meeting of the Hokkaido Section of Japan Chem. Soc., July, 1986

Measurements of Surface Oxide Films on Metallic Electrode by Using Optical Techniques; T. Ohtsuka: The '86 Seminor of the Corrosion Research Association in Hokkaido, Aug., 1986

Anodic Passivation Film on Titanium by Ellipsometry and Raman Spectroscopy ; T. Ohtsuka, J. Guo, M. Masuda and N. Sato : The 37th Meeting of the Intern. Soc. of Electrochem., Vilnius, USSR, Aug. 1986

IR Reflection and Raman Spectroscopy of the Anodic Oxide Films on Tungsten ; T. Ohtsuka, N. Goto, K. Kunimatsu and N. Sato : Intern. Conf. on Structure and Dynamics of Solid/ Electrolyte Interfaces, Berlin (West), FRG, Sept., 1986

Optical Measurements of the Surface Thin Oxide Films on Metals ; T. Ohtsuka : Seminar at Abteilung Korrosion, TU Clausthal, Clausthal-Zellerfeld, FRG, Sept., 1986

Optical and Impedance Study on Passive Film on Iron ; T. Ohtsuka : Seminar at Dept. Metallurgy and Material Sci., Uni. Nottingham Nottingham, G. Britain, Sept., 1986

Piezo-electric Response to Surface Stress Change of Iron, Nickel, and Copper Electrodes ; M. Seo, X. C. Jiang and N. Sato : The '86 Fall Meeting of the Electrochem. Soc. Japan, Sept., 1986

Surface Enrichment and Corrosion Resistivity of Alloys ; M. Seo and N. Sato : The 33rd Symposium on Corrosion and Protection, Nov. 1986

Impedance of Titanium Electrode Covered with Passive Oxide Films ; K. Azumi, T. Ohtsuka and N. Sato : *ibid.*, 1986

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

J. Kitabuki, T. Kozaki, K. Shimokuni, Y. Takemoto,
S. Tsukamoto and N. Miyazawa

The laboratory is concerned with studies on corrosion of metallic materials used in nuclear industry, physical and chemical characterizations of iron rust components, chemistry of uranium compounds, development and improvement of hydrogen reservoir alloys, and development of computer-aided, electrochemical measurements.

The following research is complete or in progress :

(1) Corrosion of SUS 304 stainless steel was studied in aqueous solutions of organic and inorganic reagents which are used for decontamination of primary water coolant circuits of nuclear reactors.

(2) Magnetite and other spinel compounds were synthesized by various preparation methods, and characterized by XRD, SEM, Mössbauer spectroscopy, and surface area measurements. The dissolution behavior of these compounds was observed in aqueous solutions of three kinds of decontamination reagent, EDTA, EDTA+ N_2H_2, and oxalic acid.

(3) The applicability of the outer-sphere complex model for the interpretation of the ionic strength dependency of stability constants of uranyl and thorium chloro-complexes was investigated.

(4) Oxidation rates were measured thermogravimetrically for the uranium dioxide specimens of three different particle sizes as functions of temperature and oxygen pressure. The reaction mechanism was interpreted by the reaction-zone model.

(5) Equilibrium and kinetic measurements were made for the hydrogen absorption and release in an $FeTi_{1.1}$ hydrogen reservoir alloy, and these behaviors were explained by considering the special features of the alloy microstucture.

(6) A computer-aided method was devised to observe and analyse various types of electrochemical transients. Under the control of a micro-processor, a cyclic potentiostatic polarization was given to a electrode, and the transient response data were treated to obtain the kinetic parameters.

Oral Presentation

Adsorption/Absorption of Chloride ion on/in Iron Passive Film; T. Mizuno and J. O'M. Bockris: The 21st Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1986

Some Kintic Aspects of Dissolution of Uranium Dioxide Fuel; H. Ohashi: The Meeting for the Cooperative Projects by Universities and the Japan Atomic Energy Research Institute, Feb., 1986.

Development of a New Transient Response Method (1) and (2); M. Moriya and T. Morozumi: The 53rd Annual Meeting of Electrochem. Soc. of Japan, Apr., 1986.

Familiar Electrochemistry; T. Mizuno: The Meeting of Hokkaido Kyohenkai Association, Apr., 1986.

A Prevention Technique for the Pulverization of the $Fe-Ti_{1.1}$ Hydrogen Storage Alloy by Electroless Copper Plating; T. Mizuno, J. Kitabuki and T. Morozumi: The Joint Spring Meeting of the Hokkaido Sections of the Japan Institute of Metals and The Japan Iron and Steel Association, June, 1986.

Dependency of Magnetite Morphology on Preparation Conditions; H. Ohashi, N. Kosai, T. Kozaki and T. Morozumi: The 1986 Summer Meeting of the Hokkaido Sections of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, July, 1986.

Behavior of Choride Ions Preceding Iron Pitting; T. Mizuno: *ibid.*, July 1986.

Ionic Strength Dependency of the Stability Constants of Uranyl and Thorium Chloro-Complexes; T. Morozumi and H. Ohashi: *ibid.*, July, 1986.

Study on Pitting Mechanism of Passivated Iron with Chloride Ions, Using Radioactive Isotope; T. Mizuno: The Joint Fall Meeting of the Hokkaido Sections of the Japan Institute of Metalls and the Japan Iron and Steel Association, Nov., 1986.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Prof. Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno
and Miss S. Akiyama

Students

I. Saeki, M. Itoh, T. Oda and M. Yamagami

Professor Nagayama reached retirement from Hokkaido University in March 1986, and moved to Nippon Chemi-con Co., Ltd. in Tokyo. Mr. Otake also retired from the university in the same month. Mr. Katayama returned to Asahikawa National College of Technology in February. Professor Furuichi was appointed to this laboratory in December.

The research projects in progress and under consideration are :
(1) Reactions between metal oxide powders.

The effect of the history of metal oxide preparation and the method of mixing oxide powders on the reactions will be examined. Thermoanalytical and surface analysis (xps) methods are planned for characterizing the oxide powders.
(2) Acid-base dissociation at metal oxide/solution interfaces.

A method was developed to determine the equilibrium constants of the reaction by analysing the titration curves for metal oxide suspensions. The values of constants were obtained for MnO_2, Fe_3O_4, etc. The values reflect the acid-base properties of the oxides prepared under different conditions. The method can be used for quality control in MnO_2 production in the dry cell industry, and for the characterization of corrosion products from metals and alloys.
(3) Adsorption of metal ions on MnO_2.

The stoichiometry and equilibria were examined for the adsorption of Zn^{2+} and Ni^{2+} ions on MnO_2. The amount of adsorbed metal ions was higher for higher metal ion concentration and pH.

An equation was established for this equilibrium relationship, and the values of the constants included were determined. The results can be used to evaluate the behavior and the role of heavy metal ions in MnO_2 dry cells. The values of the constants characterize MnO_2 prepared under different conditions.

(4) Effect of aging of hydroxide on the formation of composite oxide films on aluminum.

Composite oxide films were formed in a neutral borate solution by anodizing hydroxide-covered aluminum after aging the hydroxide under different conditions. The formation behavior of the composite oxide was examined as functions of the aging time and temperature. The effect of hydroxide-aging on the structure and formation of the composite oxide can be explained in terms of the structural change in the hydroxide during aging.

(5) Anodizing of Al-Si alloys in sulfuric acid solution.

Aluminum Silicon alloys with Si content between $0-13.5 \mathrm{wt}\%$ were anodized galvanostatically in a H_2SO_4 solution to examine the effect of the Si-content on the formation of porous anodic oxide films. With increasing Si-content in the alloy, the steady value of the anode potential and the current efficiency of oxide formation increased.

(6) Electrochemical formation of Zr-Cr and Ti-Cr composite oxide films on alloys.

A method for producing thin composite oxide layers of Zr-C or Ti-Cr on alloys was developed. The method involves the cathodic reduction of alloys in a chromate solution containing $Zr(IV)$ or $Ti(IV)$ ions. The treated Fe-Cr alloys showed good oxidation resistance in air after several thermal cycles, 20 h at 1173 K and cooling to room temperature. The method can be applied to other compositions including rare earth elements.

(7) High temperature oxidation of type 430 stainless steel in H_2O-O_2 atmospheres.

A large amount of data was accumulated for oxidation at 1173-1373 K in $0.03-0.20 \mathrm{~atm} H_2O - 0.165 \mathrm{~atm} O_2 - N_2$ atmospheres. Type 430 stainless steel showed breakaway at these conditions, and

the phenomena were considered to be a type of localized corrosion. The life time of the material (time to breakaway) showed Weibull distributions. The oxidation behavior and the effect of water vapor on breakaway can be understood from statistical considerations.

Oral Presentation

Surface Modification of Zinc with Organic Compounds to Improve Corrosion Resistance; H. Konno, Z. Zhu and M. Nagayama: The 21st Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1986.

A Thermodynamic Interpretation of Ion-Exchange Properties of Metal Oxides; H. Tamura and M. Nagayama: *ibid.*

XPS Analysis of MnO_2 Heated at 400°C; M. Mitsuta, H. Tamura and M. Nagayama: The 1986 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb., 1986

Amounts of H^+ Ions Released from the MnO_2 Surface by the Adsorption of Zn^{2+} Ions; N. Katayama, H. Tamura and M. Nagayama: *ibid.*

Formation of Voids in the Composite Oxide Films on Aluminum; H. Takahashi, Y. Umehara and M. Nagayama: *ibid.*

Effect of the Preparation Temperature of NiO on the Solid State Reaction in $NiO-TiO_2$ System; Y. Tsutsui, R. Furuichi and T. Ishii: *ibid.*

Mechanism of Void Formation in the Composite Oxide Films on Aluminum; H. Takahashi, Y. Umehara and M. Nagayama: The 73rd Meeting of Metal Finishing Soc. Japan, Mar., 1986.

Characterization of MnO_2 by Analysing the Ion-Exchange Properties; N. Katayama, H. Tamura and M. Nagayama: The 52nd Spring Annual Meeting of Japan Chemical Society, Apr., 1986.

Effect of the Pre-heating on the Duplex Structure Development of Sintered Fe_3O_4; R. Furuichi, K. Niwa and T. Ishii: *ibid.*

Reactivity of Al_2O_3 for the Solid State Reaction in $CuSO_4-Al_2O_3$ System; T. Tsuchida, Y. Tanioka, R. Furuichi and T. Ishii: *ibid.*

Effect of Aging of Hydroxide on the Formation of Composite Oxide Films on Aluminum; H. Takahashi, Y. Umehara and M. Nagayama: The 169th Meeting of Electrochem. Soc. (Boston), May 1986

Hot-water Hydration of Porous Anodic Oxide Films on Aluminum and Acid-Dissolution of Hydrated Films. I. Analysis by Gravimetric Method; M. Koda, H. Takahashi and M. Nagayama: *ibid.*

Hot-water Hydration of Porous Anodic Oxide Films on Aluminum and Acid-Dissolution of Hydrated Films. II. Analysis by Impedance Measurements; M. Koda, H. Takahashi and M. Nagayama: *ibid.*

The Effect of Water Vapor Partial Pressure on the Breakaway of SUS 430 Stainless Steel at Elevated Temperatures; I. Saeki, H. Konno and M. Nagayama: The 1986 Summer Meeting of the Hokkaido Sections of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, July, 1986.

Effect of the Mixing Method for Preparation of Powdery Reactant on the Reaction in $MO(M=Cu, Zn)-Al_2O_3$ System; K. Matsui, T. Tsuchida, R. Furuichi and T. Ishii: *ibid.*

Catalytic Activity of the Different Aluminas (η, θ, γ, δ, $\alpha-Al_2O_3$) in Isomerization Reaction of 1-Butene; K. Watanabe, T. Tsuchida, R. Furuichi and T. Ishii: *ibid.*

Aging Effect of Hydroxides on the Structure of Composite Oxide Films on Aluminum; H. Takahashi, Y. Umehara and M. Nagayama: *ibid.*

Liberation of H^+ Ions from MnO_2 Accompanied by the Zn^{2+} Ion Adsorption —Effect of Heat Treatment—; N. Katayama, H. Tamura and M. Nagayama: *ibid.*

Surface Characterization of Amalgams Using XPS; T. Hanawa, H. Takahashi, M. Ohta, R. F. Pinizzotto, J. Ferracane and T. Okabe: The IADR (Hague, Netherland), Aug., 1986.

Formation Behavior of Composite Oxide Films on Aluminum; H. Takahashi: The 2nd Meeting of Hokkaido Branch of Light Metal Inst. Japan, Sept., 1986.

Breakaway of Type 430 Stainless Steel in H_2O–O_2 Atmospheres at Elevated Temperatures; I. Saeki and H. Konno: The 33rd Annual Symposium on Corrosion and Protection, Oct., 1986.

Effect of Heat Treatment of Hydroxide on the Formation of Composite Oxide Films on Aluminum; H. Takahashi, M. Yamagami and M. Nagayama: The 7th Meeting of Metal Finishing Soc. Japan, Oct., 1986

Zn^{2+}–H^+ Ion Exchange on MnO_2; H. Tamura, N. Katayama and M. Nagayama: The 35th Annual Meeting of Japan Society for Analytical Chemistry, Oct., 1986.

Laboratory Study of Dissolution of Magnetite in Soluitons Containing Chelating Agents; S. Takasaki, H. Tamura and M. Nagayama: The 4th Int. Conf. on Water Chemistry of Nucl. Reactor Systems (Bournemouth, England), Oct., 1986.

Characterization of MnO_2; H. Tamura, M. Mitsuta, M. Nagayama and N. Katayama: The 27th Battery Symposium in Japan, Nov., 1986.

Thermoanalytical Study on the Catalytic Effect of α–Fe_2O_3 on the Thermal Decomposition of $KClO_4$; R. Furuichi and T. Ishii: Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis (Hangzhan, China), Nov., 1986.

Thermoanalytical Study on the Reactivity of Amorphous Aluminas Prepared by the Thermal Decomposition of Aluminum Chlorite and Nitrate; T. Tsuchida, R. Furuichi and T. Ishii: *ibid.*

ESCA Measurement of Thin Oxide Films on Aluminum; H. Takahashi: ARS Seminor Sponsored by Metal Finishing Soc. of Japan, Dec., 1986.

ELECTROMETALLURGY LABORATORY

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

Visiting Researcher

Masami Taguchi

Students

T. Horie, K. Miura, I. Ohira, T. Toyoda, H. Takahashi
K. Miyama and T. Yamada

Professor Ishikawa attended The First Chinese-Japanese Bilateral Symposium on Molten Salt Chemistry and Technology which was held in Shanghai, China in May 11-14, 1986. Associate Professor Narita attended Symposium on The Interaction of Molten Salts and Metals which was held in University of York, York, England in July 2-4, 1986 and on High Temperature Corrosion which was held in The University of Provence, Marseille, France in July 6-11, 1986. Dr. Sasaki attended The 37th Meeting of ISE which was held in Lithuanian SSR, Vilnius, USSR in August 24-31, 1986.

Professor Li Tiefan, Insititute of Corrosion and Protection of Metals, Academia Sinica, China, visited in July 29-30, 1986, to exchange our mutual interests on high temperature corrosion.

Mr. M. Taguchi spent his sabbatical period of 10 months for studying corrosion of titanium and titanium nitride in sulfuric acid solutions.

Research 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 alkaline earth chlorides molten salts containing $AlCl_3$ and/or $TiCl_4$ in the temperature range from

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700 to 800°C.

(2) Sulfidation-oxidation behaviors of boiler tubes in atmospheres encountered in oil fired boilers. Sulfidation and reduction behavior of the pre-formed oxide scales on a STBA24 was investigated at 973 K in the H_2S-H_2 atmosphere.

(3) The ceramic-metal bondings : bondings of Si_3N_4 and stainless steel with Ni-Ti filler and of Al_2O_3 and nickel with Cu and W plates as interlayers were developed and evaluated their mechanical properties.

(4) Corrosion and inhibition mechanism of copper and its alloys with nitrogen containing organic inhibitors have been investigated by electrochemical techniques, a conventional optical microscope, SEM and EPMA. The accelerated pitting test cell, developed by BNF Metals Technology Centre, are being applied for the determination of Type II pitting propensity of supply waters. The Type II pitting is a prevalent type of pitting corrosion in copper tubes in Japan.

(5) A stacked rotating bipolar electrode cell is being tested for the electrochemical treatment of dilute cyanide solution containing heavy metal. The fundamental studies on recovery of gallium from Bayer solution are in progress.

(6) 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

Electrowinning of Liquid Aluminum from Chloride Melts in the Five-stacked Bipolar Electrode Cell with 300 Ampere ; K. Nishimura, S. Konda, T. Narita and T. Ishikawa : The 12th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1986.

Electrolysis of Dilute Cupric Sulfate with a Stacked Rotating Bipolar Electrode Cell — a Scaled up Cell— ; T. Sasaki and T. Ishikawa : *ibid.*, Jan., 1986.

The Role of Chromium Carbides on the Grain Boundary Sulfidation ; T. Narita and T. Ishikawa : The 21st Annual Meeting of the

Corrosion Research Association in Hokkaido, Jan., 1986.

Corrosion Problems and Its Preventive Measure of Writing Goods ; T. Notoya and T. Ishikawa : *ibid.*, Jan., 1986.

Corrosion Test of Carbon Steel in Tap Water of the Flow Circuit ; R. Hatazawa, S. Konda and T. Ishikawa : *ibid.*, Jan., 1986.

Effect of Phytic Acid on the Anodic Behavior of Brasses ; T. Notoya and T. Ishikawa : The 1986 Winter Meeting of the Hokkaido Section of Jap. Chem. Soc., Feb., 1986.

Application of Pipe-stacked Wall to the Self-heating Simulated Bipolar Electrode Cell ; S. Konda, T. Narita and T. Ishikawa : The Meeting of Research Projects, Grant-in-Aid for Scientific Research (Energy), Feb., 1986.

Electrowinning of Highly Purified Aluminum from Fused Chloride Melts ; A. Sato, S. Konda, T. Narita, T. Ishikawa : The 53rd Annual Meeting of Electrochem. Soc. of Japan, Apr., 1986.

Electrochemical Treatment of Cupric Sulfate Solution with a Stacked Rotating Bipolar Electrode Cell (Part 7) Electrolysis with a 120 mm Diameter Cell ; T. Sasaki and T. Ishikawa : *ibid.*, Apr., 1986.

High Temperature Corrosion of Boiler Tubes —Part 1— Corrosion Behavior of Boiler Tubes in H_2S–H_2 Atmopsheres ; T. Narita, T. Ishikawa and Y. Harada : The 98th Spring Meeting of JIM, Apr., 1986.

Scale Structures of Oxide Scales on Co–Mn Alloys ; T. Narita and T. Ishikawa : *ibid.*, Apr., 1986.

Reaction between Silicon Nitride Ceramics and Metals ; T. Takashima, T. Yamamoto, T. Narita and K. Nishida : *ibid.*, Apr. 1986.

Interlayer for the Stress Relief of the Ceramic-Metal Bondings ; T. Yamamoto, T. Takashima, T. Narita and K. Nishida : *ibid.*, Apr., 1986.

Effects of Phytic Acid and Calcium Phytate on the Anodic Behavior of Brasses ; T. Notoya and T. Ishikawa : The 52nd Spring Meeting of Japan Chemical Society, Apr., 1986.

Fundamental Study on Electrowinning of Liquid Aluminum from

Chloride Melts; T. Ishikawa, T. Narita and S. Konda: The First China-Japan Joint Seminar on Chemistry and Technology of Fused Salts, May, 1986.

Anodic Behavior of alpha-Brass in Boric-Borate Solution with Phytic Acid and Calcium Phytate; T. Notoya and T. Ishikawa: '86 Spring Meeting of the Japan Soc. of Corrosion Engineering, May, 1986.

Effect of Diffusion-annealing on the Layer Structures of the Ceramic-Metal Bonding Layers with a Ti–Ni Filler; K. Miura, T. Narita and T. Ishikawa: The Hokkaido Section Meeting of JIM, June, 1986.

Study on Electrowinning of Titanium Containing Alloys from the $TiCl_4$-Melts; T. Horie, S. Konda, T. Narita and T. Ishikawa: The Meeting of The Light Metal Hokkaido Section, July, 1986.

Sulfidation Properties of Chromium and Chromium-bearing Alloys at Elevated Temperatures; T. Narita and T. Ishikawa: International Symposium on High Temperature Corrosion (Marseille, France), July, 1986.

On the Diffusion Limiting Current in a Stacked Rotating Bipolar Electrode Cell; T. Sasaki and T. Ishikawa: The 1986 Summer Meeting of the Hokkaido Section of Japan Chem. Soc., July, 1986.

Copper Recovery in a Stacked Rotating Bipolar Electrode Cell; T. Sasaki and T. Ishikawa: The 37th ISE Meeting, Aug., 1986.

Effect of Dissolved Constituents in Tap Water on the Corrosion Behavior of Steel Pipes; R. Hatazawa, S. Konda and T. Ishikawa: The 33rd Annual Symposium on Corrosion and Protection, Oct., 1986.

Purification and Its Limitation of Aluminum Chloride by the Sublimation Method; S. Konda, T. Narita and T. Ishikawa: The 1986 Fall Meeting of the Electrochem. Soc. Japan, Oct., 1986.

Effect of Phytic Acid on Corrosion of Zinc; T. Notoya and T. Ishikawa: The 53rd Fall Meeting of Japan Chemical Soc., Oct. 1986.

Corrosion Inhibition of Brasses in Benzyl Alcohol and Oleic Acid;
    T. Notoya: The 26th Meeting of Japan Copper and Brass
    Research Association: Nov., 1986.
Development of Aluminum Electrowinning Process with Chloride
    Melts and Bipolar Electrode Cell (Part 10) The 300 Ampere
    Operation of the Self-heating Simulated Cell with Five Units;
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Piezoelectric Response to Surface Stress Change of Platinum Electrode

Masahiro Seo, Takamitsu Makino
and Norio Sato

The peizoelectric detection has been proved sensitive to surface stress change of platinum foil electrodes in sulfate solutions of various pH values and sodium hydroxide solution. Electrocapillary-like curves were successfully obtained from the measured peizoelectric signals as a function of potential. The potential of electrocapillary maximum decreases linearly with pH at the rate of $-40\,\mathrm{mV/pH}$. The potential of electrocapillary minimum found in the anodic potential scan was 0.35 V more positive than the equilibrium potential of PtO/Pt system. It appears that the electrocapillary minimum is connected with a reconstruction or place exchange step of the oxygenated platinum surface corresponding to PtO monolayer. (English)

Application of Laser Raman Spectroscopy to the Corrosion Study

Toshiaki Ohtsuka

The laser Raman spectroscopy was reviewed on its application to the study of metallic corrosion. The laser Raman spectroscopy may be one of the promising methods to dectect the compositions of corrosion films on metals under in-situ conditions. The following examples of measurements have been introduced : (1) Assignment of iron rust, (2) In-situ measurement of the oxide layer thermally formed in gaseous environments, (3) In-situ measurement of the oxide layer anodically formed in aqueous solution, and (4) Surface-enhanced-Raman-scattering (SERS) spectra of BTA inhibitor adsorbed on cupper. (Japanese)

Pulsed Anodic Reactions

Hidetaka Konno

The Theory and Practice of Pulse Plating, Ed. by J-C.
Puippe, and F. Leaman, American Electroplaters
and Surface Finishers Society, Orlando,
Florida, p. 209 (1986)

Theoretical and practical aspects of pulsed anodic reactions are
introduced and reviewed briefly. Much emphasis is placed on
anodizing of aluminium. (English)

Electrochemical Behavior and Surface Composition of Copper Containing Ferritic Stainless Steel in Sulfuric Acid Solution

Jiaju Guo, Masahiro Seo, Yoshitaka Sato,
Gunnar Hultquist, Christofer Leygraf
and Norio Sato

Electrochemical behavior and surface composition of ferritic stainless steels (Fe-26Cr-0.4Cu and Fe-26Cr) in $1.0 \, \text{mol} \cdot \text{dm}^{-3}$ sulfuric acid solution have been investigated to evaluate the effect of copper-addition on the corrosion resistivity of ferritic stainless steel. The addition of copper suppressed significantly the dissolution current density of the steel in the active potential region. The surface enrichment of metallic copper for the steel subjected to active dissolution was revealed by Auger electron spectroscopy (AES).

The second and small anodic current peak for the steel containing copper appeared at 0.32 V (SHE) in the passive potential region. From the linear relation between the electric charge, Q_1, required for active dissoliton and the electric charge, Q_2, corresponding to the area of the second peak, it is confirmed that the second peak is caused by anodic dissolution $(Cu \rightarrow Cu^{2+} + 2e)$ of metallic copper enriched on the steel surface. From the measurements of the potential decay curve after 1 h-passivation and of the reactivation potential by a cathodic potential sweep of the passivated steel, it is found that copper has a detrimental effect on the passivity of ferritic stainless steel. (Japanese)

The Influence of Minor Alloying Elements (Nb, Ti and Cu) on the Corrosion Resistivity of Ferritic Stainless Steel in Sulfuric Acid Solution

Masahiro Seo, Gunnar Hulquist, Christofer Leygraf and Norio Sato

The effect of the minor alloying elements (Nb, Ti and Cu) and of Mo on the corrosion resistivity of ferritic stainless steel (Fe–26Cr alloy) was investigated in 1.0 mol dm^{-3} sulfuric acid solution with or without 0.5 mol sodium chloride, based on potentiodynamic polarization, potential decay and reactivation potential measurements. Surface characterization of the ferritic stainless steel subjected to active dissolution or passivated was performed with simultaneous use of Auger electron spectroscopy and an argon-ion sputter-etching technique. Copper and molybdenum suppressed the anodic dissolution of the steel. Copper and niobium were significantly enriched on the steel surface during active dissolution. A chromium enrichment was always found in the passive film of all the investigated steels. No enrichment of the other alloying elements was observed in the passive film and the substrate. Niobium, titanium and molybdenum stabilized the passive film, whereas copper had a detrimental effect on the passivity. The influence of the alloying elements on the corrosion resistivity of the steel is discussed in relation to the surface analytical results. (English)

A Role of Chloride Ions in Pitting
Corrosion of Iron

Tadahiko Mizuno

The adsorption of chloride ions on iron in borate buffer solution have been studied using radiotracer technique.

The results obtained are summarized as follows :

(1)   The adsorption of chloride ions occurs on bare iron and passive iron surfaces with an increase of the potential.

(2)   The amount of the adsorption of chloride ions, $\varGamma$, increases linearly with concentration of Cl^- in the solution.

(3)   The minimum concentration of NaCl electrolyte required to cause breakdown of passive film on iron surfaces was found to be $1 \, mol/m^3$, which corresponds to about $8 \times 10^{-6} \, mol/m^2$ of chloride ions concentration on iron surfaces.   The higher NaCl concentration in solutions and the larger amount of chloride ions on iron surfaces are needed at lower electrode potentials.

(4)   Penetration mechanism of chloride ions for the iron passive film breakdown hardly explains the experimental details.   (Japanese)

Adsorption and Absorption of Chloride
Ions on Passive Iron Systems

V. Jovancicevic, J. O'M. Bockris, J. L. Carbajal,
P. Zelenay and T. Mizuno

The adsorption and absorption of chloride on iron in borate buffer solution have been studied using a radiotracer technique. The two processes are clearly distinguishable by their different time constants, ~ 1 min for adsorption and ~ 1 h for absorption. The adsorption of chloride on bare iron and passive layer surfaces follows the Tempkin type of isotherm. The free energy of adsorption of chloride on passive layer is significantly higher than that on bare iron. Partial charge transfer between adsorbed chloride ion and Fe^{2+} and/or Fe^{3+} on the passive surface has been proposed to account for this difference. The "saturation" coverage of chloride on passive layer varies with concentration and attains a value of 0.8 at higher concentrations. The absoprtion of chloride into the passive layer starts at about -0.1 V/NHE, followed by a linear increase with the potential. The steady-state value of absorption of chloride at the breakdown potential varies with concentration of chloride in the solution and breakdown potential. The maximum value of absorption before breakdown occurs is $\theta = 2.5$. (English)

The Accelerated Pitting Test for Copper Tubes to Determine Pitting Propensity of Supply Waters

T. Notoya and T. Fujii

BNF Metals Technology Centre has been developed an accelerated pitting test cell for the determination of a waters capability to support Type I pitting of copper. The electrochemical cell can be set up on a bench, requires two litres of test water and gives a result within 5 days. Merits of use of the electrochemical cell, method of operation, Type I pitting mechanism, the cell assembly and interpretation of the results are described. (Japanese)

Laboratory Study of Dissolution of Magnetite in Solutions Containing Chelating agents

S. Takasaki, H. Tamura and M. Nagayama

In connection with the chemical decontamination technology, a study of dissolution of magnetite in EDTA or citrate solutions with different pH has been carried out. The dissolution rates reached a maximum value at pH 2 with EDTA, and at pH 4 with citrate. This means that there are optimum pH in the chemical decontamination with these chelating agents. It was found that these optimum pH coincide with the pH where the adsorption of anionic species of chelating agents on magnetite is maximum. (English)

Surface Modification of Zinc with Organic Compounds as a Means for Improving Corrosion Resistance

Hidetaka Konno, Zufang Zhu
and Masaichi Nagayama

It was found that organic compounds which can form insoluble complexes with zinc in aqueous solutions may modify zinc surfaces to be resistant to corrosion. Two surface modification methods using 8-hydroxyquinoline [HQ] were found to improve corrosion resistance. In one method (the CT method) zinc is immersed in a neutral solution containing a small amount of HQ, and in the other (the SA method) zinc is anodized in the same type of solution. After CT, the surface consisted of bis(8-hydroxyquinolato)Zn(II) [ZnQ_2] which is insoluble in water but soluble in alcohol, and the corrosion of zinc was inhibited at an efficiency of about 90% in aerated chloride media of $pH = 4-10$. The surface modified by SA was complex ; the outer part was mainly composed of ZnQ_2 and soluble in alcohol, while the inner part which was insoluble in organic solvents consisted of an upper layer of complexes of Zn (II)–HQ-derivatives and a bottom layer of Zn(II)-oxyhydroxide. The inner part formed by SA showed good corrosion resistance even after removal of the outer part. The surfaces produced by CT and SA could be useful as an undercoat for paint, and CT can be used as a temporary protection of zinc as washing with alcohol will restore the metallic luster. (Japanese)

Bronze Disease

Takenori Notoya

On ancient bronzes, buried more than thousand years, carry copper- and tin-oxides and a green patina of basic salts, such as nantokite, malachite, azurite, atacamite, brochantite and others. This patina may be described as extremely protective, but damage was found in the articles in British museums. The trouble was apparently due to acetic acid absorbed from the wood shavings as packaging materials. It would seem that the acetic acid penetrated through original cracks present in the patina and attacked the substrate copper, producing soluble acetate, which was converted to basic carbonates or basic sulphates and acetic acid liberated. The acetic acid attacked further on the bronze article resulted in collapse of the patina layer. The recurrence of attack by aggressive species is called "bronze disease". A few examples similar to the bronze disease appeared in Japan are also described. (Japanese)

Inhibition of 70/30 Brass Dezincification by Water-Soluble Organic Inhibitors

Takenori Notoya

Boshoku Gijutsu, **35**, No. 9, 615 (1986)

Five different types of copper or zinc complexing agents as water-soluble dezincification inhibitors for 70/30 brass were tested by using a potentiostatic acceleration technique in 0.5 M NaCl solution containing an acetic acid-sodium acetate buffer solution of pH 4.43 at 60°C. Effectiveness of the inhibitors for preventing anodic dissolution of copper and zinc from 70/30 brass was in the following order ; phytic acid < octylhydroxamate potassium salt < thioglycolic acid < dimethyldithiocarbamic acid sodium salt < benzotriazole. The inhibition mechanism of these inhibitors is probably due to the formation of copper and/or zinc complex films on the alloy surface. It is concluded that an addition of the most promising inhibitors such as benzotriazole to corrosive environments is an alternative method to prevent dezincification attack of 70/30 brass. (English)

ABSTRACTS

Evaluation of Phytic Acid as a Corrosion
Inhibitor for Copper

Takenori Notoya

Journal of the Japan Copper and Brass Research
Association, **25**, 21 (1986)

Phytic acid $(C_6H_{18}O_{24}P_9)$ is widely distributed in wild plants
and grains, and can be extracted from rice bran. Recently it is
found that pitting attack in copper tubes can be prevented by small
addition of phytic acid as low as 0.1 ppm to hot water supply
systems. The present study deals with effects of phytic acid on
anodic polarization behavior of copper as compared with those of
benzotriazole in borate solutions. Experiments were carried out in
$Na_2B_4O_7$–H_3BO_3 solutions with Pt sheet as a counter electrode.
Anodic polarization was made potentiostatically stepwise 20 mV in
every minute from a corrosion potential up to 0.90 V vs S. C. E.
in unstirred solutions with and without inhibitor at 60°C. The
amount of copper dissolved in the solution was determined by using
atomic absorption spectrophotometry. The anodic reactions of cop-
per in the solution are characterized current peaks followed by
decreasing current which are related to anodic dissolution of copper,
Cu_2O formation and further oxidation of Cu_2O to CuO or $Cu(OH)_2$.
In the presence of phytic acid or benzotriazole the anodic current
peaks decreased with increasing concentration of the inhibitor in
the borate solution of pH 9.2 where maximum inhibition efficiency
for phytic acid and benzotriazole were 35.2 and 99.4% at 10^{-2} M,
respectively. The inhibition efficiency depends on inhibitor con-
centration and pH of the solution. Acceleration of copper anodic
dissolution was observed in the borate solutions of pH 8.5, 6.9 and
6.5 at phytic acid concentrations above 10^{-3} M, suggesting formation
of soluble compounds of Cu-phytic acid. Inhibition action of phytic
acid would be attributed to the formation of cupric-phytate chelating
layer on underlying Cu_2O/Cu surface. Advantage and disadvantage
of phytic acid in relation to practical application as compared with
benzotriazole are described. (Japanese)

Corrosion Inhibition Mechanisms of Benzotriazole Related Inhibitors and Their Applications

Takenori Notoya

Published by Japan Association of Corrosion Control (1986)

The 44 page brochure presents a chronological review of corrosion inhibition mechanisms of benzotriazole and its derivatives for copper, copper alloys and other metals. The role of underlying copper oxide films present on the metal surfaces is discussed in the inhibition action of the inhibitors. Also covered are physico-chemical data on benzotriazole and its related inhibitors. The author provides wide range of applications of the inhibitors based on the latest technical literature. (Japanese)

Acid-Base Properties of MnO$_2$ with and without Heat Treatment

H. Tamura, M. Mitsuta and M. Nagayama

Manganese dioxide suspended in aqueous solution is covered with acid and base surface hydroxyl groups, $\equiv$MnOH(a) and $\equiv$MnOH(b). Dissociation of these groups forms negative and positive sites on the oxide surface, $\equiv$MnO$^-$ and $\equiv$Mn$^+$. In this investigation, the difference in the surface concentrations of the charged sites, that is, the surface charge density, σ, was measured by acid-base titration for manganese dioxide samples with and without heat treatment. The pH at which $\sigma=0$ (pzc) for the heat treated sample was higher than that for the as received sample. An equation was derived for the relationship between σ and pH by considering the electrostatic effect of σ on the dissosiation. The equation well fitted to the experimental data, and the values of the acid dissociation constant of $\equiv$MnOH(a), K_a, and the base dissociation constant of $\equiv$MnOH(b), K_b, were determined. It was found that K_a decreases while K_b increases by the heat treatment of the oxide. The pzc is given by pzc$=($pK_a+pK_w-p$K_b)/2$, where K_w is the ionic product of water, and p represents $-$log functions. The increase in pzc by the heat treatment is ascribed to both the increase in pK_a and the decrease in pK_b. (English)

Ion-Exchange Characteristics of Manganese Dioxide

H. Tamura, M. Mitsuta and M. Nagayama

Two kinds of MnO_2 samples, prepared by electrochemical and chemical processes, were suspended in NaOH solutions containing $NaNO_3$, and the suspensions were titrated with HNO_3. The results were analysed by considering the following ion exchange reactions at two different surface hydroxyl sites

$$\equiv MnOH_a + Na^+ \rightleftharpoons \equiv MnO^- \cdot Na^+ + H^+$$

$$\equiv MnOH_b + NO_3^- \rightleftharpoons \equiv Mn^+ \cdot NO_3^- + OH^-$$
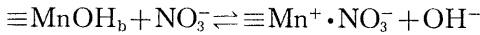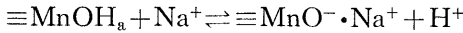
where $\equiv MnOH_a$ acts as an acid and $\equiv MnOH_b$ as a base, and $\equiv Mn^+$ and $\equiv MnO^-$ are the charged sites to which NO_3^- and Na^+ are adsorbed. The net surface charge density $\sigma = [\equiv Mn^+] - [\equiv MnO^-]$, was estimated from the results of the titration. The equilibrium conditions of these reactions can be expressed by the following equations with exponential terms including σ

$$K_a = \frac{[\equiv MnO^- \cdot Na^+] \, a_H}{[\equiv MnOH_a] \, [Na^+]} \cdot \exp(-A_a \cdot \sigma)$$

$$K_b = \frac{[\equiv Mn^+ \cdot NO_3^-] \, a_{OH}}{[\equiv MnOH_b] \, [NO_3^-]} \cdot \exp(A_b \cdot \sigma)$$

The values of the constants, K_a, K_b, A_a and A_b, were determined by a non-linear regression analysis of experimental data, and the ion-exchange characteristics of the two MnO_2 samples were discussed in terms of the values of the constants. (Japanese)

Adsorption of Zn^{2+} Ions on MnO_2 with and without Heat Treatment

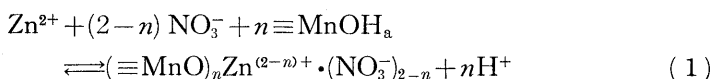H. Tamura, N. Katayama, T. Nakai
and M. Nagayama

For MnO_2 samples with and without heat treatment, the amount of Zn^{2+} ions adsorbed was measured as a function of Zn^{2+} ion concentration and solution pH. The surface concentration of adsorbed Zn^{2+}, Γ, was higher with increasing $[Zn^{2+}]$ and pH. The heat treated MnO_2 adsorbed less amount of Zn^{2+} ions than the unheated MnO_2. An equation was derived for the equilibrium relationship between Γ, $[Zn^{2+}]$, and pH by considering that 1) the adsorption occurs by exchanging protons in acid hydroxyl groups on the surface of MnO_2, and 2) further adsorption is retarded by the previously adsorbed Zn^{2+}. The equation well explained the experimental data, and based on the values of the equilibrium constants, the effect of heat treatment on the adsorption was discussed. (English)

Equilibria of Adsorption of Zinc Ions on Manganese Dioxide

Hiroki Tamura, Kunimichi Sasaki, Tohru Nakai,
Noriaki Katayama and Masaichi Nagayama

The behavior of adsorption of Zn^{2+} ions on MnO_2 was investigated to establish the stoichiometry and the equilibrium conditions of the reaction. The concentrations of Zn^{2+} ions in solution were determined by atomic absorption spectrophotometry, and the amount of Zn^{2+} ions adsorbed was obtained from the difference between the concentrations before and after the adsorption. The surface concentration of adsorbed Zn^{2+} ions, Γ, increased with increasing pH and the concentration of Zn^{2+} ions in solution, $[Zn^{2+}]$. The adsorption is considered to occur by exchanging n protons in the acid hydroxyl groups on the surface of MnO_2, $\equiv MnOH_a$, with a Zn^{2+} ion :

$$Zn^{2+} + (2-n) NO_3^- + n \equiv MnOH_a$$
$$\rightleftharpoons (\equiv MnO)_n Zn^{(2-n)+} \cdot (NO_3^-)_{2-n} + nH^+ \qquad (1)$$

The reaction product is a surface complex with a charge of $2-n$, to which NO_3^- ions are adsorbed as counter anions. The equilibrium condition of this reaction is given by

$$\beta_n = \frac{\Gamma [H^+]^n}{[Zn^{2+}] [NO_3^-]^{2-n} [\equiv MnOH_a]^n} \exp(B\Gamma) \qquad (2)$$

where β_n is the equilibrium constant and B is a constant. The exponential term expresses the retardation of adsorption by the adsorbed Zn^{2+} ions. By multiparametric curve-fitting, the values of β_n, B, and n were determined to be : $\beta_n = 3.45 \times 10^{-3} mol^{-0.79} m^{2.2}$, $B = 1.83 \times 10^6 mol^{-1} m^2$, and $n = 1.21$ for an ionic strength of 0.1 ($NaNO_3$) and at 25°C. Γ calculations from eq. (2) agreed well with the measured Γ over wide ranges of $[Zn^{2+}]$ and $[H^+]$. (Japanese)

Historical Approach to Passivity

Norio Sato

The article deals with historical development of the study of metallic passivity. It was J. Keir in 1790 who for the first time described passivity of iron in concentrated nitric acid. Later, anodic passivity of iron was found. K. F. Bonhoeffer and his colleagues in 1950's succeeded in measuring the anodic polarization curve of iron involving passivation in acid solution by use of a potentiostat. Since then, a number of potentiostatic anodic polarization curves of various metals and alloys in different environments have been established, which have so far contributed greatly to the progress in corrosion prevention of metals. Definition of the metallic passivity was once the subject of debate, and C. Wagner in 1965 gave the passivity two kinds of definitions from thermodynamic and kinetic standpoints of view. In the past twenty years evidences have been presented of the existance of a thin surface oxide film on passivated metals and alloys. Recently, the semiconductor property of the passive film has received attention in understanding the nature of passivity. (Japanese)

Raman Spectra of the Anodic Oxide Film on Titanium in Acidic Sulfate and Neutral Phosphate Solutions

T. Ohtsuka, J. Guo and N. Sato

Laser Raman spectroscopy has been applied under *in situ* and *ex situ* conditions to the anodic oxide films formed on titanium at various potentials in neutral phosphate and acidic sulfate solutions. The Raman spectra reveal that the anodic oxide film is primarily composed of an anatase type of TiO_2. From the relation between the Raman band intensity, film thickness, and surface morphology, it is likely that the film changes from the amorphous state to the crystalline state beyond a certain critical potential. (English)

Spectroscopic Photoresponse of the Passive Film Formed on Iron

Kazuhisa Azumi, Toshiaki Ohtsuka and Norio Sato

Spectroscopic photoresponse of the passive film formed on iron in neutral borate solution was studied. The spectroscopic three parameter reflectometry and the photoelectrochemical technique were employed to obtain the spectra of absorption coefficient and photocurrent. From these spectra, a conversion efficiency, η, from the flux of photons absorbed in the film to the photocurrent was calculated as a function of photon energy. The result shows that the photoexcitation process of electron-hole-pair formation includes two transition mechanisms; a direct allowed transition and an indirect allowed tranition. The direct transition, which occurs in the photon energy higher than 2.6 eV, is attributed to the excitation between the valence (O-2p) and the conduction (Fe-3d) bands of iron oxide, whereas the indirect transition, which occurs in the photon energy higher than 0.8 eV, is associated with electronic levels of impurities or $d-d$ transition in the passive film. The maximum value of η observed at a photon energy of 3.1 eV is about 20%, and this high efficiency suggests that the high electric field exists in the passive film of iron. (English)

Impedance of Iron Electrode Passivated
in Borate and Phosphate Solutions

Kazuhisa Azumi, Toshiaki Ohtsuka and Norio Sato

The semiconductive properties of the passive film on iron were investigated by measuring the impedance of iron electrode in borate and phosphate solutions at various pH values. The impedance data were compared with the thickness data previously obtained from 3-parameter reflectometry. From the effect of frequency and potential on the impedance an equivalent circuit is postulated for the passivated iron electrode, which consists of a series connection of two parallel $R-C$ circuits. One component R_L-C_L of the two parallel circuits which predominates over frequencies lower than 100 Hz, characterizes the dielectric property of the passive film, whereas the other component R_H-C_H which appeares at higher frequencies corresponds to the oxide/solution interface. From comparison of C_L with the film thickness, the passive film is found to consist of an inner electron-conductive layer where no potential drop occurs and an outer carrier depletion layer where the electric field is of the order of $1 \times 10^8 \, Vm^{-1}$. The dielectric constant of the outer layer is also evaluated at about 40. The component R_H-C_H is sensitive to the anionic species present in the solution and is thus likely to be assosiated with an ionic adsorption-desorption process taking place across the electric double layer at the oxide/solution interface. (English)

Hot-Water Hydration of Porous Anodic Oxide Films on Aluminum and Acid-Dissolution of Hydrated Films
Part 1. Analysis by Gravimetric Method

M. Koda, H. Takahashi and M. Nagayama

Proc. Symp. Aluminium Surface Treatment
Technology, p. 355 (1986)

Porous oxide films formed in an oxalic acid solution were hydrated in hot water at 99.5°C and then dissolved in a chromic acid-phosphoric acid solution. The weight-time characteristics of the specimen was measured during these successive experiments and the results were analyzed as a function of the initial film thickness and the time of hydration. The function of hydration in increasing the protective ability of film is explained. (English)

Hot-Water Hydration of Porous Anodic Oxide Films on Aluminum and Acid-Dissolution of Hydrated Films

Part 2.   Analysis by Impedance Measurements

M. Koda, H. Takahashi and M. Nagayama

Porous oxide films formed anodically on aluminum were hydrated with hot water at 99.5°C and then dissolved in a chromic acid-phosphoric acid solution.   During these experiments, the time-variation of impedance was measured to examine the changes in film structure.   The equivalent circuit of hydrated films was found to consist of the capacitance, C_B, of the barrier oxide layer, combined in series with a parallel combination of capacitance and resistance components, C_H and R_H, of the hydrated oxide in the pores.   The changes in C_h^{-1}, R_H and C_b^{-1} with time agree quite well with those expected from the gravimetric analysis.   (English)

Effect of Aging of Hydroxide on the Formation of Composite Oxide Films on Aluminum

H. Takahashi, Y. Umehara and M. Nagayama

Aluminum specimens covered with hydroxide were aged in dry air at different temperatures and for different periods, and then anodized in a neutral borate solution to form 'composite oxide films' with amorphous and crystalline oxide layers. The 'relaxation' (loss of high voltage-supporting ability) of the composite oxide was examined by keeping the specimens on open circuit in the borate solution, and by reanodizing with a small constant current after 'relaxation'. The distribution of imperfections in the oxide was estimated by analyzing the potential-time curves during reanodizing.

It was found that aging causes a retardation of the transformation of amorphous oxide into crystalline oxide during anodizing. The composite oxides formed with aging have a large number of imperfections which can easily be relaxed and repaired. The imperfections in the oxide formed with aging distribute at high concentrations in the crystalline oxide near the amorphous oxide layer and near the original boundary between the crystalline and amorphous oxide layer. The oxide formed without aging showed no concentrated region of imperfections in the region near the original boundary between the crystalline and amorphous oxide layer, and was relaxed only with extreme difficulty.

The aging effects described above on the imperfection distribution and the relaxation characteristics were enhanced when increasing the aging period and decreasing the aging temperature. (English)

Structure and Formation Mechanism of Composite Oxide Films on Aluminum

Hideaki Takahashi

Pure aluminum specimens covered with hydroxide films were anodized galvanostatically in a neutral borate solution at different temperatures to form composite oxide films. The formation behavior was examined by electrochemical measurements, chemical analysis and electron microscopy.

It was found that the composite oxide films consist of two layers ; an outer crystalline oxide layer (thickness δ_0) and an inner amorphous oxide layer (δ_i). During anodizing, δ_0 increased with anodizing time t_a, at a rate increasing with t_a. The rate of increase in δ_i decreased with t_a. The behavior of δ_0 and δ_i became more pronounced at higher anodizing temperature, T_a.

Formation mechanism of the composite oxide film is discussed in terms of the ion transport, the viod formation and the current efficiency for the oxide formation. (Japanese)

Raman Spectroscopy of Thin Corrosion Films on Iron at 100 to 150 C in Air

T. Ohtsuka, K. Kubo and N. Sato

Laser Raman spectroscopy (LRS) has been applied for the detection and characterization of thin corrosion films formed on iron in air at a temperature range from 100 to 150 C. In situ ellipsometric measurements have also been conducted for quantitative estimations of the film growth kinetics. It is found that (1) the oxidation of iron in dry air leads to the formation of a surface oxide film composed primarily of magnetite and (2) the water vapor in air accelerates the formation of hematite. The ratio of magnetite to hematite in the surface oxide film appears to increase with (1) increasing water vapor pressure, (2) ascending temperature, and (3) extending oxidation time. (English)

Selective Oxidation of Fe-30 Cr at Low
Temperatures: 743-823 K

Masahiro Seo, Gunnar Hultquist, Fumio Baba
and Norio Sato

Fe-30 Cr specimens were oxidized for $6 \times 10^2 - 3.6 \times 10^4$ s at 743-823 K in pure oxygen at a pressure of 1.33×10^4 Pa. Depth profiling of oxidized surfaces was performed with the simultaneous use of Auger electron spectroscopy (AES) and inert gas-ion (Ar^+, or Xe^+) sputter-etching technique. Chromium was selectively oxidized, and a chromium-depletion zone was formed in the underlying alloy. The values (10^{-16}–10^{-15} cm^2 s^{-1}) of the interdiffusion coefficient, $\tilde{D}$, of the underlying alloy evaluated from the depth-composition profiles were compared in magnitude with the values extrapolated from lattice diffusion data of the corresponding alloy obtained at high temperature. The apparent activation energy obtained from an Arrhenius plot of the evaluated diffusion coefficient, however, was one-third of the value for the corresponding alloy at high temperatures. Discussion was made on the possible mechanism of selective oxidation at low temperatures. (English)

Selective Oxidation of FeCr Alloys in the 295-450 K Temperature Range

Gunnar Hultquist, Masahiro Seo and Norio Sato

A series of iron-chrominum alloys were oxidized for 10^2 to 6×10^4 s in air and in the 295-500 K temperature range. Room-temperature oxidation of iron, chromium, antimony, and copper were also conducted at extended times. Oxidation characteristics such as oxide thickness and composition of the oxide and of the underlying alloy were evaluated from measurements by electron spectroscopy for chemical analysis (ESCA). An initial selective oxidation of chromium with a concomitant chromium depletion in the alloy was found. This initial oxidation step is followed by growth of an outer, iron rich oxide which causes the former chromium depletion to vanish. Apparent activation energies extracted from parabolic oxidation kinetics (295-500 K) of the investigated metals were found to be in the 10-20 kcal/mole range. (English)

Stacked Rotating Bipolar Electrode Cell for Recovery of Copper from Dilute Cupric Sulfate Solution

Takeshi Sasaki and Tatsuo Ishikawa

A novel bipolar electrode cell, which we refer to as a stacked rotating bipolar electrode cell, has been developed for recovery of heavy metals from dilute solutions. The cell consists of two feeder electrodes and four stator bipolar electrodes alternating with five rotor bipolar electrodes. Fins are mounted on the anode surfaces to promote turbulence and scrape of the deposited copper. The characteristics were studied in batch operation of powdery copper recovery from cupric sulfate solutions in the concentration range from 500 to 10 ppm Cu^{2+}. A high recovery speed is achieved due to the excellent stirring effect of the rotating electrodes and the increase in micro-turbulence at the large active surface caused by the deposition of powdery copper. The high speed electrolysis and the large surface area per unit cell volume as attained by stacking the bipolar electrodes also lead to a high space time yield. (English)

The Effect of a Powdery Copper Layer on the Electrolysis of Cupric Sulfate Solution in a Stacked Rotating Bipolar Electrode Cell

Takeshi Sasaki, Yuji Shinno and Tatsuo Ishikawa

The effect on the rate of electrolysis of a predeposited powdery copper layer on the electrodes in a stacked rotating bipolar electrode cell was studied in dilute cupric sulfate solutions. Polarization curve measurements and the electrolysis of 30 l of 100 or 500 ppm Cu^{2+} solutions were carried out with electrodes covered with powdery copper layers formed under various conditions.

The rate of electrolysis is promoted remarkably by the powdery copper and the higher speed is attributed to increase in surface micro-turbulence with increases in the active surface area. It is concluded that a powdery copper layer predeposited on electrodes enables high speed electrolysis, and the optimum pre-electrolysis conditions for the layer are proposed. (English)

TG and DTA Studies on the Thermal Decomposition
of KClO$_4$-α-Fe$_2$O$_3$ Mixtures

Ryusaburo Furuichi, Yasuhide Tsusaka, Tadao Ishii
and Takeshi Okutani

The catalytic effect of α-Fe$_2$O$_3$ on the thermal decomposition of KClO$_4$ was studied by TG and DTA methods. The ferric oxide was prepared from FeC$_2$O$_4\cdot$2H$_2$O by its thermal decomposition in air. DTA and TG curves showed that the addition of α-Fe$_2$O$_3$ led to an acceleration effect on the solid-state decomposition of KClO$_4$. The acceleration effect increased with a decrease in the preparation temperature and an increase in the mixing ratio of α-Fe$_2$O$_3$. From TG curves, the rate constant, k, was estimated by assuming a first-order rate law. An Arrhenius plot of k showed a straight line, which had a sharp bend at the temperature, T_B, characteristic of the respective α-Fe$_2$O$_3$ sample. It was suggested that the solid-state decomposition proceeded below T_B and the liquid-state decomposition above T_B. The fraction of KClO$_4$ decomposed in the solid state, α_B, was estimated to be 0.03 for pure KClO$_4$. The α_B value for the sample mixed with α-Fe$_2$O$_3$ prepared at 1000, 750 and 500°C was 0.065, 0.07 and 0.39, respectively. The increase in mixing ratio resulted in an increase in α_B: α_B=0.06 for 1% α-Fe$_2$O$_3$, 0.16 for 10%, 0.26 for 30% and 0.39 for 50%. The activation energy of the solid-state decomposition, E_s, of pure KClO$_4$ was 78.4 kcal mol^{-1} and those of KClO$_4$+α-Fe$_2$O$_3$ mixtures were 53.6, 60.2 and 60.8 kcal mol^{-1} for the oxide prepared at 500, 750 and 1000°C, respectively. The change in mixing ratio of the oxide did not show any effect on E_s. The activation energy of the liquid-state decomposition, E_l, for pure KClO$_4$ was 151.4 kcal mol^{-1} and those of KClO$_4$+α-Fe$_2$O$_3$ mixtures were in the range 147.8–155.4 kcal mol^{-1}. Changes in the preparation temperature and the mixing ratio of α-Fe$_2$O$_3$ did not give a systematic influence on E_l.
(English)

Effect of Procedures Used for Mixing Powdery Reactants on $ZnFe_2O_4$ Formation

Ryusaburo Furuichi, Katsuhito Tani,
Kazuyoshi Kamada and Tadao Ishii

The formation of $ZnFe_2O_4$ was studied by using two $\alpha\text{-}Fe_2O_3$ and two ZnO powder samples. These oxides were mixed in an agate mortar and a vee mixer in different mixing ratios (R). The graph of fraction reacted (α) versus R was U-shaped with the minimum α value at $R = 40-60\%$. The samples prepared by mortar mixing showed higher α values than those prepared in the vee mixer. Scanning electron micrographs revealed that the mortar mixing resulted in $\alpha\text{-}Fe_2O_3$ particles densely covered with small comminuted ZnO particles, in contrast to mixing in the vee mixer, which resulted in point contacts between the particles, which retained the original particle shape and size before mixing. The relationship between α and R and the difference in α values obtained by the two mixing procedures could be explained on the basis of the contact area. Mixing in the vee mixer was concluded to be suitable for use in the reactivity test on $\alpha\text{-}Fe_2O_3$ powder based on $ZnFe_2O_4$ formation, because this procedure resulted in point contacts between the reactant particles and in a smaller change in particle size. (English)

Electroless Copper Plating for Preventing Pulverization of FeTi$_{1.1}$ Hydrogen Storage Alloy

Tadahiko Mizuno, Jun-ichi Kitabuki
and Takashi Morozumi

An electroless copper plating technique was proposed to prevent the pulverization of FeTi$_{1.1}$ hydrogen storage alloy due to the repeated hydrogen absorption and desorption. The Saubestre (II) solution was utilized as a plating reagent, which was composed of $CuSO_4$, NaOH, formalin and Rocelle salt. The plating procedure was so simple that a reasonably uniform coating of 0.2μm in average thickness was easily obtained by dipping the hydrogenated specimen in this plating solution for 5 ks at 295 K.

Such treated specimens achieved almost perfect inhibition of pulverization even after 5000 cycles repeated absorption and desorption. The copper plating scarcely influenced the equilibrium absorption and desorption isotherms, but it retarded the rapid absorption of the hydrogen unbeared alloy with the mass flow mechanism.

The latter effect ceased by the change of reaction mechanism at lower temperature. No initial activation was needed for the copper-plated alloy. (Japanese)

Ionic Strength Dependency of Stability Constants of Uranyl and Thorium Chloro-Complexes

Takashi Morozumi and Hiroshi Ohashi

Stability constants, K_{st}, of uranyl and thorium chloro-complexes decrease rapidly with increasing ionic strength. The ionic complexes are typical outer-sphere complexes, as the Fuoss formula is applicable to this relationship and the heat of formation is remarkably small. The inter-ionic distance of 1.9×10^{-8} and 4.0×10^{-8} cm were obtained for the uranyl and thorium chloro-complexes. The thermodynamic equilibrium constants of 33 and $212 \, mol^{-1} l$ were also determined for these chloro-complexes. The relatively low K_{st} values, which have been found for higher ionic strengths by previous investigators, are explained by the same outer-sphere complex model. The upper limit of the complexation was estimated as a function of ionic strength on the basis of the above model. (Japanese)

Collimator Efficiency in Laser Vaporization Systems Using Mass Spectrometric Detection

H. Ohashi, S. K. Yagnik and D. R. Olander

High-temperature vaporization characteristics of refractory solids are often investigated using laser pulse heating and mass spectrometric detection. The geometry of the vaporizing surface, collimator, and the detector is an important consideration in interpreting such experimental results. The mass spectrometer signal depends on the radial dependence both in the laser beam power density and of the relative effectiveness of off-center radial positions on the surface in contributing to the total signal. The function characterizing the latter effect is called the collimator function. Its measurement and application to a typical laser evaporation experimental system has been described. (English)