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CONTENTS

Passive Film and Anodized Oxide Film :

Sulfidation :

Metal Physics and Mechanical Properties :

Electrometallurgy :

Miscellaneous :

ELECTROCHEMISTRY LABORATORY

Prof. Dr. N. Sato, Assist. Prof. Dr. M. Seo
Dr. T. Ohtsuka and Ms. J. Fujiwara

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Students

K. Azumi, F. Baba, N. Goto, K. Kubo,
Y. Sato and T. Makino

The research activities of the laboratory continue to be directed towards a better understanding of the molecular processes involved in the corrosion and passivation of metals and semiconductors from the fundamental view points.

Passivity and Passivity Breakdown

Basic research has been devoted to studies of the process of passivation, the growth and structure of passive oxide films, the local breakdown of passivity, and the local corrosion process taking place at the passivity breakdown sites. Particular attention has been paid to the molecular fluctuation of the passive oxide film which would be enhanced by the adsorption of aggressive anions.

Surface Analysis of Metals and Alloys

Auger electron spectroscopy (AES) combined with argon ion-sputter etching has been used for the study on selective oxidation of iron-chromium alloy in a low temperature range. Particular attention has been paid to the alloy depletion profiles in connection with selective oxidation of chromium component. Surface characterization by AES has been performed of ferritic stainless steels with minor alloying elements (Ti, Nb and Cu) subjected to active dissolution or passivation in sulfuric acid solution to examine the corrosion resistance.

Surface Stress Measurement of Metal Electrodes

The change in surface stress of platinum foil electrodes in sulfate solutions of different pH has been measured as a function of electrode potential by using a piezo-electric detector with a potential-modulation technique. The potential of zero charge (PZC) of platinum electrodes and the pH dependence of PZC were evaluated from the surface stress curve (electro-capillary curve). This technique of the surface stress measurement is being applied to the passivated iron electrode.

Optical and Impedance Technique for Passivated Iron

The passivation film on iron has been studied by the 3-parameter-spectroscopic reflectometry and the impedance measurements. The complex refractive index, thickness and dielectric property of the film were deduced as a function of potential and solution pH. The semiconductive properties of the film were also discussed from the result of absorption spectra, impedance measurements, and photo-induced current measurements.

Laser Raman Spectroscopy for Corrosion Study

Laser Raman spectroscopy has been used to identify the composition of surface corrosion film formed on iron at temparature 100∼150°C in air containing water vapor. It was found that the dry-air oxidation leads to the formation of Fe_3O_4 as a main product and that the wet-air oxidation however accelerates the formation of α-Fe_2O_3. Laser Raman spectroscopy was also applied to the study of the surface passivation film formed on a compound semi-metal, HgTe, in aqueous solution.

Other Activities

In 1983, Prof. Sato and Dr. Ohtsuka attended the 5th International Symposium on Passivity held in Bombannes, France, from May 30 to June 3 and presented two papers on the passive film on iron and nickel. Dr. Ohtsuka then participated in the International Conference on Ellipsometry and the Optical Methods for Surface and Thin Film Analysis held in Paris from June 7 to 10 and presented a poster paper on the reflection-spectroscopic method for analysis of thin surface films. Dr. Ohtsuka afterwards stayed in Clausthal-Zellerfeld, FRG, from June 11 to August 10 to make a joint work on the passivation film with Prof. Dr. K. E. Heusler. Prof. Sato attended the 1983 fall meeting of the Electrochemical Society held in Washington, USA from Oct. 9 to 14. At the meeting he was given the Outstanding Achievement Award from the Corrosion Division of the Electrochemical Society and gave an award lecture on the ion-permeability of corrosion precipitate films. Dr. Seo visited the Royal Institute of Technology in Stockholm, Sweden, in November, 1983, for Japan-Sweden collaboration research and gave a lecture on the quantitative surface analysis of the passive film at a seminar held in the Swedish Corrosion Institute. He also visited New-castle Upon Tyne Polytechnic, Corrosion and Protection Centre at UMIST, and further participated in the 3rd International Conference on Quantitative Surface Analysis held in Teddington, UK, from November 22 to 24 to present a paper on the depth-profiling of oxide film/metal interfaces.

In 1984 Prof. Sato visited the Corrosion Section of the Royal Institute of Technology in Stockholm, Sweden, on March 18–30 to promote a collaborative study on the passivity of iron-base alloys supported by JSPS. Dr. Sakashita moved to the Fundamental Research Laboratories of Nippon Steel Coorporation, April 1st, 1984. Prof. Sato and Dr. Seo visited Toronto, Canada, to present three papers at the 9th International Congress on Metallic Corrosion held on June 3～7. After the Congress, Prof. Sato visited National Research Council of Canada in Ottawa for a week and Dr. Seo paid a visit to the Royal Institute of Technology in Stockholm, Sweden, for about two week to conduct a joint research on the passivity of iron-base alloys. Prof. Sato participated in the International Society of Electrochemistry 35th Meeting held in Berkeley, California, U. S. A., on August 5～10, 1984, to present an invited paper at the section of electrochemical energy conversion.

The following scientists from over the sea paid the visit to this laboratory in the year of 1984: Professor J. O'M. Bockris from Texas A & M University, U. S. A., on April 17～18; Dr. G. Hultquist from the Royal Institute of Technology, Sweden, on July 28-Aug. 25; Professor K. E. Heusler from the Technical University of Clausthal, West Germany, as a visiting professor supported by JSPS for 45 days from July 2 to August 15; Professor E. Heitz from DECHEMA-Institute, West Germany, on September 17∼18, Professor J. H. Block from Fritz-Haber Institute of Max-Plank-Gesellschaft on September 20; Dr. C. Hinnen from C. N. R. S., France, on October 4; Dr. R. O. Lezna from INIFTA, Laplata, Argentina, on October 18; Dr. Chen Jing Ming from Shanghai Institute of Metallurgy, China, on October 31-November 3.

Oral Presentation

Selective Surface Oxidation of Fe–30 Cr Alloy in the Low Temperature Range (673 K 873 K); F. Baba, M. Seo and N. Sato: The 19th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 18, 1984

Measurements of Surface Oxide Film on Metal by Laser Raman Spectroscopy; T. Ohtsuka, N. Goto, M. Sakashita, M. Seo and N. Sato: The 19th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 18, 1984

Crevice Corrosion and Volume Transport through Porous Iron (III) Hydroxide Membranes; T. Shimakura, M. Sakashita and N. Sato: The 10th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan. 17, 1984

The Ion Permeability of Corrosion Precipitate Films and Its Role in Metallic Corrosion; N. Sato: Seminar on Japan-Sweden Collaboration Research, Stockholm, Sweden, March 20, 1984

Selective Surface Oxidation of Iron-base Alloy and Concentration Distribution in the Underlying Alloy; M. Seo, F. Baba and N. Sato: The Spring Meeting JIM, April, 2, 1984

Composition Change of Anodic Oxide Film on Titanium due to the Cathodic-Reduction Treatment; T. Ohtsuka, M. Masuda and N. Sato: The 51th Annual Meeting of Electrochem. Soc. of Japan, April, 1984

Selective Surface Oxidation of Binary Alloy and Interdiffusion of

Substrate Alloy; M. Seo, F. Baba and N. Sato: '84 Spring Meeting of the Japan Society of Corrosion Engineering, May, 18, 1984

Impedance and Photo Response of Passivation Film on Iron; K. Azumi, T. Ohtsuka and N. Sato: '84 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1984

Application of Laser Raman Spectroscopy to Measurements of Surface Oxide Films on Metals; T. Ohtsuka, N. Goto, M. Sakashita, M. Seo and N. Sato: '84 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1984

Ion Selectivity and Electro-osmose in Porous Precipitate Films of Hydrated Iron (III) Oxide; M. Sakashita, T. Shimakura and N. Sato: 9th International Congress on Metallic Corrosion, Toronto, Canada, June 4, 1984

Potential-pH Diagram of Composition/Structure of Passive Film on Iron; R. Nishimura and N. Sato: 9th International Congress on Metallic Corrosion, Toronto, Canada, June 4, 1984

An Auger Study on Selective Surface Oxidation of Ni-Cr Alloys; M. Seo and N. Sato: 9th International Congress on Metallic Corrosion, Toronto, Canada, June 5, 1984

Measurements of High Temperature Oxidation Film on 18-8 Stainless Steel by Laser Raman Spectroscopy; N. Goto, T. Ohtsuka, M. Seo and N. Sato: The Spring Meeting of the Hokkaido Section of JIM, June, 1984

Passivity of Metallic Titanium; N. Sato and T. Ohtsuka: International Society of Electrochemistry 35th Meeting-Berkeley, California U. S. A., August 5, 1984

Spectra of the Thin Surface Oxide Films Anodically Formed on Iron and Titanium by In-situ Reflectometry; T. Ohtsuka, K. Azumi and N. Sato: The 13th Congress of International Commission for Optics, Sapporo, Japan, August 20-24, 1984

Raman Spectroscopy Applied to the Oxide Films Formed on Metals in Air and in Aqueous Solution; T. Ohtsuka, N. Goto and N. Sato: The 9th International Conference on Raman Spectroscopy, Tokyo, Japan, August 27-September 1, 1984

Corrosion Precipitate Membranes Leading to Passivation of Metals; N. Sato and M. Sakashita: The Fall Meeting of the Japan Institute of Metals, Oct. 9-11, 1984 Hiroshima

Case Study of Corrosion in Dental Diagnosis; K. Matsuda, H. Sakai, H. Shimokobe: 31 Annual Symposium on Corrosion and Protection, Oct. 14-16, 1984, Yokohama

Measurement of Change in Surface Stress of Metal Foil Electrode; M. Seo, T. Makino and N. Sato: The Fall Hokkaido Section Meeting of JIM, Nov. 16, 1984

Selective Surface Oxidation of Fe-Cr Alloy and Formation of Cr-Depletion Layer in the Substrate; F. Baba, M. Seo and N. Sato: The Fall Hokkaido Section Meeting of JIM, Nov. 16, 1984

Analysis of Cr-Depletion Layer Formed in the Substrate by Selective Surface Oxidation of Fe-Cr Alloy in a Low Temperature Range; M. Seo F. Baba and N. Sato: The 4th Discussion Meeting of the Japan Society of Surface Science, Dec. 6, 1984

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Assist. Prof. Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno, Mr. Y. Otake,
S. Takasaki, H. Iwata and Miss A. Matsuno

Students

K. Ebihara, K. Mabuchi, T. Shigekuni, M. Mitsuta,
I. Saeki, T. Nakai and N. Sato

Current research in this laboratory is mainly concerned with the anodic oxidation of aluminum, corrosion of iron and steels, analysis of metal and oxide surfaces, and the chemistry at metal oxide/solution interfaces.

Mr. Takasaki from Kurita Water Industries Ltd. joined our group in Apr. 1983, and returned to his firm in May 1984. Mr. Umehara from Nippon Gakki Seizo Co. Ltd. joined our group in Jul. 1984.

The main research projects completed or in progress are as follows :

(1) Chemical conversion film on aluminum

Hydrous oxide films were formed on aluminum by immersion it in boiling distilled water or amine-containing solution and examined by gravimetry, electron microscopy and a. c. impedance measurements. The chemical conversion films were found to consist of three layers : A porous fibril outer layer, relatively dense inner layer and very thin innermost layer at the film/metal interphase.

(2) Formation mechanism of porous anodic oxide films on aluminum

Porous type anodic oxide films were formed on aluminum in oxalic acid solution under different temperatures, current densities, and the concentrations of oxalic acid to examine the morphology and the density of the films using electron microscopy, gravimetry, and electrochemical measurements. In has been found that the anodizing potential, i. e. the electric field in the barrier layer, is responsible for the film geometry.

(3) Field-assisted dehydration of hydroxide films on aluminum

Aluminum specimens covered with a hydrous oxide film were anodized in a neutral borate solution to examine the formation mechanism of oxide films. During anodizing, the hydrous oxide films were dehydrated to form a crystalline oxide layer, and also an amorphous oxide layer were formed at the oxide/metal interphase.

(4) Dissolution of iron oxides in chelating solutions

Specifically, dissolution of magnetite in EDTA solutions was examined to establish the technological fundamentals of chemical decontamination of nuclear energy power plants. The effect of pH and EDTA concentration on the dissolution behavior can be explained by considering equilibria of 1) release of Fe ions from magnetite, 2) chelation of Fe ions with EDTA, and 3) air oxidation Fe (II) species.

(5) Acid-base dissociation at MnO_2/solution interfaces

To characterize MnO_2 samples for dry cell use, the acid-base dissociation of surface hydroxyl groups, $\equiv$MnOH, (release of H^+ and OH^- ions to form $\equiv MnO^-$ and $\equiv Mn^+$) was examined. Effect of pH and coexisting salt ($NaNO_3$) on the dissociation is explained by using a modified equilibrium equations in which the electrostatic interaction between releasing H^+ and OH^- ions and the surface charge is taken into consideration. Also, Zn^{2+} ion adsorption on MnO_2 is being examined.

(6) Corrosion of iron in high temperature water

The corrosion rate of iron in pure, high temperature water is measured by gravimetry, and the surface oxide films formed are examined by XPS, and X-ray diffraction.

(7) Effect of water vapor on high temperature oxidation of SUS 430 stainless steel

SUS 430 stainless steel (16 Cr steel) was oxidized at 1100°C in O_2/N_2 atmospheres containing water vapor at different partial pressures. The behavior was followed by a gravimetry and the formed oxide films were examined by XPS, SEM, EDAX, and GDS as a function of oxidation time.

(8) Descaling process of Fe-Cr alloy.

The Fe-Cr alloys having different Cr content (1~30 mass%) were oxidized at 1100°C in air containing 0.2 atm water vapor and the formed oxide films were removed successively by mechanical and chemical processes. The descaling behavior was followed by a gravimetry, XPS, SEM, and EDAX to understand the significance of each process.

(9) Anodizing of copper and zinc with organic compounds

Copper and zinc specimens were anodically treated in a neutral borate solution cantaining small amount of organic compounds. Compositions and protective abilities of the resulted surfaces were examined.

Oral Presentation

The Control of the Structure of Porous Anodic Oxide Films on Aluminum ; H. Takahashi : Symposium on the New Application of Anodic Oxide Films on Aluminum, Sponsored by Japan Institute of Light Metals, Mar. 1984

Anodizing of Aluminum Covered with a Hydrous Oxide films. ; H. Takahashi and M. Nagayama : The 19th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1984

Current-Voltage Characteristics at anodizing of aluminum in Acid Solutions ; K. Ebihara, H. Takahashi and M. Nagayama : The 10th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1984

Determination of Acid-Base Sites on MnO_2 Surfaces ; H. Tamura, M. Mitsuta and M. Nagayama : The 1984 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb. 1984.

Estimation of Structure of Porous Anodic Oxide Films on Aluminum by the "Pore-Filling" method ; H. Takahashi and M. Nagayama : *ibid.*, Jan. 1984

Anodic Treatment of Steel with Organic Compounds ; H. Konno, M. Oda, M. Nagayama and H. Leidheiser, Jr. : The 69th Annual Meeting of the Metal Finishing Society of Japan, Mar. 1984

Estimation of Morphology of Two-Layered Porous Oxide Films on Aluminum by the "Pore-Filling" Method.; H. Takahashi, H. Kumagai and M. Nagayama: *ibid.*, Mar. 1984

Theoritical Explanation on the Current-Voltage Characteristics at Anodizing of Aluminum; K. Ebihara, H. Takahashi and M. Nagayama: *ibid.*, Mar. 1984

Acid-Base Reactions of Surface Hydroxyl Groups on MnO_2; H. Tamura, M. Mitsuta and M. Nagayama: The 49th Spring Annual Meeting of the Chemical Society of Japan, Apr. 1984

Dissolution of Magnetite in EDTA-Containing Solutions; S. Takasaki, H. Tamura and M. Nagayama: The 1984 Annual Meetting of the Japan Society of Corrosion Engineering, May 1984

Breakdown of Oxide Films on Aluminum in Neutral Solutions Containing Organic and Inorganic Anions; H. Takahashi, M. Mukai and M. Nagayama: 9th Int. Cong. Metallic Corrosion (Toronto, Canada), Jun. 1984

Corrosion of Carbon Steel in High Temperature Water and the Structure of Surface Oxide Films; Y. Horii, K. Mabuchi, H. Konno, H. Takahashi and M. Nagayama: *ibid.*

Dissolution Behavior of Iron Oxides in Acidic Solutions Containing EDTA; S. Takasaki, H. Tamura and M. Nagayama. The Water Chemistry Committee Meeting of the Atomic Energy Society of Japan, July 1984

Corrosion of Carbon Steel in High Temperature Water; M. Nagayama: Seminar sponsored by the Committee of Japan Atomic Energy, Aug. 1984

Promotive Effect of EDTA on the Dissolution of Iron Oxides; H. Tamura, M. Nagayama and S. Takasaki: The 45th Analytical Chemistry Symposium, July 1984

Structure Change of Porous Anodic Oxide Films on Aluminum During hot Water Treatment; M. Nagayama: Seminar Sponsored by Aluminum Section of Metal Finishing Society of Japan, Jun. 1984

Mechanism of Sealing of Porous Anodic Oxide Films on Aluminum; M. Nagayama: Seminar at Greneral Research Institute for Non-Ferrour Metals, Beijing, China, Sept. 1984

On the Mechanism of Anodizing of Aluminum; M. Nagayama: Zhejiang Technical Institute, Hanzhou, China, Sept. 1984.

Anodizing of Aluminum in Acid Solution; M. Nagayama: Shanghai Metallugical Institute, Sinica Academy, Shanghai, China, Sept. 1984

Analysis od Solid Surface by XPS; H. Konno: A Seminar by the Hokkaido Branch of the Japan Institute of Metals, Mar. & Sep. 1984

Oxidation of SUS 430 Stainless Steel at 1100°C in a Moist Atmosphere; H. Konno, T. Shigekuni and M. Nagayama: The 31st Annual Symposium on Corrosion and Protection, Oct. 1984.

Proton Dissociation at MnO_2/Solution Interfaces; H. Tamura, M. Mitsuta and M. Nagayama: The 25th Battery Symposium in Japan, Nov. 1984

MnO_2 Surfaces and Zn^{2+} ion Adsorption on MnO_2; M. Nagayama and H. Tamura: The 5th Meeting on Dry-cell Materials, Nov. 1984

Determination of Oxide Films on Aluminum in Aqueous Solution; H. Takahashi, T. Toda and M. Nagayama: The 70th Annual Meeting of the Metal Finishing Sciety of Japan, Nov. 1984

ELECTROMETALLURGY LABORATORY

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

Students

Y. Shinno, N. Nishimura, R. Hatazawa, N. Kanai,
H. Sadamitsu and S. Negishi

Research subjects in progress are as follows.

(1) Laboratory scale tests in bipolar electrode cells for electrowinning of liquid aluminum are being carried out by using alkali and alkaline earth chlorides molten salts containing aluminum chloride in the temperature range from 700° to 800°C.

(2) Stacked rotating bipolar electrode cell is being tested for recovery of copper from dilute cupric sulfate and treatment of cyanide-containing effluents.

(3) Inhibition mechanisms of localized corrosion in copper and copper base alloys with different types of organic inhibitors are being studied by electrochemical techniques and electron microscopy.

(4) 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.

Dr. T. Narita, who was formerly an instructor in the High Temperature Metal Chemistry Laboratory, joined as an Assistant Professor in May, 1984. His research subjects cover the high temperature corrosion of alloys in sulfidizing atmospheres and development of the ceramic-metal bondings.

Dr. T. Notoya attended 9th International Congress on Metallic Corrosion in Toronto, Canada on June 3~7, 1984. On returning from 9ICMC he had a seminar at the University of British Columbia where he spent a two-year sabbatical working on corrosion inhibition.

Oral Presentation

Precise Determination of Decomposition Voltage of the $AlCl_3$ Containing Melts; H. Tanaka, S. Konda and T. Ishikawa: The 10th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan., 1984

Experimental Approarch for Design of Bipolar Electrode Cells; M. Okazaki, S. Konda and T. Ishikawa: *ibid.*, Jan., 1984

Effect of Accumulation of Deposited Copper on the Electrolysis Rate of Stacked Rotating Bipolar Electrode Cell in Cupric Sulfate; Y. Shinno, T. Sasaki and T. Ishikawa: *ibid.*, Jan., 1984

Evaluation of Corrosion Inhibitors for Dezincification of Brasses; T. Notoya and T. Ishikawa: The 19th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1984

Sulfidation Kinetics and Hexagonal Pit Formation on Sulfide Scale on Pure Chromium Metal; T. Narita and K. Nishida: *ibid.*, Jan., 1984

The Effect of Alloying Element on Corrosion Behavior of Iron Based Alloys in SO_2 Atmospheres at High-Temperature; K. Kurokawa, M. Kishimoto, T. Narita and K. Nishida: *ibid.*, Jan., 1984

Electrical Conductivity of Chloride Melts Embedded in the Alumina Particles Packed Layer; K. Nishimura, S. Konda and T. Ishikawa: The 51st Annual Meeting of Electrochem. Soc. of Japan, Apr., 1984

Electrochemical Treatment of Cupric Sulfate Solution with Stacked Rotating Bipolar Electrode Cell (Part 5). Effect of Deposited Powdery Copper on Electrode Surface; Y. Shinno, T. Sasaki and T. Ishikawa: *ibid.*, Apr., 1984

On the Bondings of SiC Ceramics and SUS 304 Stainless Steel with Al-filler; T. Narita, T. Yoneda and K. Nishida: The Spring Meeting of the Japan Inst. Metals, April, 1984

The Effect of Al on the Corrosion Behavior of Fe-Cr-Ni Alloys in SO_2 Atmospheres; K. Kurokawa, M. Kishimoto, T. Narita and K. Nishida: *ibid.*, April, 1984

On the Hexagonal Pits Grown on the Sulfide Scale on Chromium; T. Narita and K. Nishida: *ibid.*, April, 1984

Inhibition Action of Organic Inhibitors for Dezincification of Alpha Brass; T. Notoya and T. Ishikawa: '84 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1984

Evaluation of Corrosion Inhibitors for Dezincification of 60/40 Brass; T. Notoya and T. Ishikawa: 9th International Congress on Metallic Corrosion, June, 1984

Inhibition of the Dezincification of Brasses; T. Notoya: Seminar at the University of British Columbia, June, 1984

On the Bondings of Si_3N_4 Ceramics and Fe-26Cr Alloy with Ti-Ni Filler; A. Kumatoritani, K. Kurokawa, T. Narita, K. Nishida and R. Nagasaki: The Hokkaido Section Meeting of the Japan Inst., Met., June, 1984

Internal Corrosion of Steels in SO_2 Atmospheres; K. Kurokawa, T. Narita, K. Nishida and R. Nagasaki: *ibid.*, June, 1984

Corrosion Behavior of Alloys under Mechanical Deformation at High-Temperatures; T. Narita: The 55th Symposium on Corrosion and Protection, June, 1984

The Effect of Creep Deformation on Sulfidation Properties of Fe-26Cr Alloy in H_2S-H_2 Atmospheres at Elevated Temperature; T. Narita, H. Kato and K. Nishida: The Hokkaido Section Meeting of JIM, June, 1984

Development of the Cell Materials and Structure for the Self-Heating Simulated Bipolar Electrode Cell; T. Ishikawa and S. Konda: The Meeting of Research Projects, Grant-in-Aid for Scientific Research (Energy), July, 1984

Development of Stacked Rotating Bipolar Electrode Cell for Recovery of Heavy Metals from Dilute Solutions; T. Sasaki, Y. Shinno and T. Ishikawa: '84 Hokkaido Section Summer Meeting of Japan Chem. Soc., Jul., 1984

On the Recovery of Heavy Metals from Dilute Solutions using Stacked Rotating Bipolar Electrode Cell; T. Sasaki, Y. Shinno and T. Ishikawa: The 1984 Fall Meeting of the Electrochem. Soc. Japan, Oct., 1984.

Development of Aluminum Electrowinning Process with Chloride Melts and Bipolar Electrode Cell (Part 5) Experimental Determination of Design Parameters for Bipolar Electrodes; M. Okazaki, S. Konda and T. Ishikawa: *ibid.*, Oct., 1984

The Effect of Creep-Deformation on Grain Boundary Sulfidation of Fe–Cr Alloys; T. Narita, T. Ishikawa and K. Nishida: The Fall Meeting of Japan Inst. Met., Oct., 1984

The Effect of Preformed Oxide Films on the Corrosion of Fe-high Ni Alloys in SO_2 Atmospheres; K. Kurokawa, T. Narita, R. Nagasaki and K. Nishida: *ibid*, Oct., 1984

Development of Aluminum Electrowinning Process with Chloride Melts and Bipolar Electrode Cell (Part 6) The Effect of Wall Materials on Performability of Self-Heating Simulated Cell; S. Konda and T. Ishikawa: The 17th Symposium on Molten Salt Chemistry, Nov., 1984

Some Aspects on Development of Bipolar Electrode Cell used for Electrowinning of Aluminum from Chloride Melts; K. Nishimura, S. Konda, T. Narita and T. Ishikawa: The 1st Hokkaido Center Meeting of Japan Intstitute Light Metals, Nov., 1984

Prevention of Dezincification in 70/30 Brass by Corrosion Inhibitors; T. Notoya: The 24th Meeting of Japan Copper and Brass Research Association Nov, 1984

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

Prof. Dr. R. Nagasaki, Assist. Prof. K. Atarashiya
Dr. K. Kurokawa and Mr. K. Sugawara

Students

A. Kumatoritani, K. Yamamoto, T. Yoneda, I. Kosuga
S. Konya, K. Nishiyama and S. Watanabe

Prof. Nishida reached the retirement age in March, but he is busy working as a director of the Japan institute of Metals and the metal finishing society of Japan. He was succeeded by Dr. Nagasaki who came of Japan atomic energy research institute. Dr. Narita was rised to an assist. prof. of the electrometallurgy laboratory in May.

This laboratory is concerned with the studies on the metal-ceramic bonding, metal-ceramic interaction, sintering of ceramics, inter-diffusion in oxides, and high temperature corrosion of metals and alloys. The research subjects in progress are as follows:

(1) Metal-ceramic bonding: Bonding experiments between Si_3N_4 and Fe–26Cr stainless steel using Ti foil and Ni sheet as a filler were carried out in He gas atmosphere over the temperature range of 1150～1350°C. 3-point bending strength of the test specimens were measured, and the reaction zone was characterized by X-ray diffraction, EPMA, and SEM-EDAX.

(2) Metal-ceramic interaction: The chemical interaction between titanium and Si_3N_4 was investigated over the temperature range of 900～1100°C. The reaction products were TiN and Ti_5Si_3, and the growth rate of reaction zone were also measured.

(3) Sintering of Si_3N_4: Foundamental experiments of the sintering of Si_3N_4 with aluminium alkoxide and Y_2O_3 powder is being

investigated. Aluminium alkoxide is more effective than Al_2O_3 powder for sintering of Si_3N_4.

(4) Inter-diffusion : A series of the diffusion studies in oxides are being investigated experimentally. Inter-diffusion behavior between Fe_2O_3 compact and single crystal of Al_2O_3 was studied with Pt-marker at high temperatures.

(5) High temperature corrosion of metals and alloys : A series of the high temperature corrosion of metals and alloys in oxygen- and sulfur-containing gas atmospheres are being investigated. The relationship between internal sulfidation depth and Ni concentration in Fe-25Cr-Ni alloys was investigated at 900°C in H_2S-H_2 atmosphere. Furthermore, the oxidation behavior of the presulfidized Fe-25Cr-Ni alloys was investigated.

Oral Presentation

Study on SiC to SUS 304 Bonding with a Filler of Al ; T. Narita, T. Yoneda and K. Nishida : The Spring Meeting of the Japan Inst. Met., April, 1984

Effect of Al on the Corrosion Behavior of Fe-Cr-Ni-Al Alloys in SO_2 Gas Atmospheres ; K. Kurokawa, T. Narita and K. Nishida : *ibid*, April, 1984

Study on the Hexagonal Pit Formed in Chromium Sulfide Scale ; T. Narita and K. Nishida : *ibid*, April, 1984

Study on Si_3N_4 to Fe-26Cr Stainless Steel Bonding with the Filler of Ti-Ni ; A. Kumatoritani, K. Kurokawa, T. Narita, K. Nishida and R. Nagasaki : The Hokkaido Section Meeting of the Japan Inst. Met., June, 1984

Comment on the Chemistry Textbook of High School —What Process and Operation is the Sublimation ?— ; K. Atarashiya : The 49th Spring Meeting of the Japan Chemical Society, April, 1984

Effect of Creep Deformation on the High Temperature Corrosion of Stainless Steels in H_2S-H_2 Atmospheres ; T. Narita, H. Kato and K. Nishida : *ibid*, June, 1984

On the Internal Sulfidation in High Temperature Corrosion of Iron-based Alloys in SO_2 Atmospheres; K. Kurokawa, T. Narita, K. Nishida and R. Nagasaki: *ibid*, June, 1984

Effect of Preoxidized Scale on High Temperature Corrosion of High Ni Steels in SO_2 Atmospheres; K. Kurokawa, T. Narita, R. Nagasaki and K. Nishida: The Autumn Meeting of the Japan Inst. Met., Oct., 1984

Study on Si_3N_4 to Fe–26Cr Stainless Steel Bonding; A. Kumatoritani, K. Kurokawa, T. Narita, R. Nagasaki and K. Nishida: *ibid.*, Oct., 1984

Crystal Growth Phenomena in Inter-Diffusion of Al_2O_3–Mn_3O_4 System; K. Atarashiya, R. Nagasaki and K. Nishida: The Hokkaido Section Meeting of the Japan Inst. Met., Nov., 1984

Chemical Diffusion of Quasi-Binary Al_2O_3–Mn_3O_4 System in Air; K. Atarashiya, R. Nagasaki and K. Nishida: The 1984 International Chemical Congress of Pacific Basin Societies, Dec., 1984

ENGINEERING MACHINERY MATERIALS LABORATORY

Prof. Dr. K. Nagaoka, Assist. Prof. Dr. T. Noguchi,
Mr. N. Shiramine, Mr. M. Souma
and Mr. M. Fujita

Students

K. Kegasawa, K. Watanabe, K. Kamada, T. Iizuka,
I. Kōshi, I. Yamada, N. Kihira
and K. Kobayashi

Recent works in this laboratory are mainly conducted on mechanical and thermal properties of gray cast iron for machinery uses, and some works are carried on heat treatings of steel and sintered iron.

Assist. Prof. T. Noguchi was awarded with the Kusaka Prize of the Japan Foundrymen's Society in May 1984, which was founded newly for prospective research activities in the foundry. Prof. K. Nagaoka attended the Third International Symposium on the Physical Metallurgy of Cast Iron held in Stockholm in Aug. 1984, and presented a paper on the irreversible carbon diffusion in growth of cast iron. Assist. Prof. T. Noguchi went on leave in Sept. 1984 to work with Prof. Wallace at the Case Western Reserve University, Cleveland, Ohio.

Researches in progress are as follows:

(1) Fatigue fracturing of flake and nodular cast iron loaded tension cyclically was examined not only on S–N relations but also on crack propagation and fractographs. The fractography was applied on the fatigue specimens interrupted at halfway life and broken at liquid nitrogen temperature.

Fatigue fracture of cast iron progresses in a mixed mode of dimple, cleavage and striation. Paying attention to the fracture mode of pearlite in the micro-fractographs and the fractional area of graphite the fatigue in flake cast iron can be distinguished from other types of fracture.

(2) Tension tests using sub-size specimens with diameter 8, 2, and 1 mm were carried out on a low grade cast iron FC 15 in comparison to a high grade iron FC 25 tested before. Average tensile strength of 2 mm specimen was lower by about 12.5% than that of 8 mm specimen with wider scattering. Strength of the 1 mm specimen was undetermined owing to a great scattering.

(3) Mechanical properties of a medium carbon steel quenched from temperatures between A_1 and A_3 critical points were examined to clarify the brittleness of heat-treated steel. Impact strength of the steel with dual phases due to the insufficient heating was lowered markedly compared to the tempered martensite steel with same hardness and strength.

(4) Growth in austenite temperature region of gray cast iron was tested in air with reduced oxygen concentration micro-electrically, and the promotion of growth resulted was attributed to a self-carburization caused by reactions of penetrated oxygen and graphite flakes.

(5) Unified theory of growth mechanism in cast iron was considered to be originated in the irreversible carbon diffusion between metallic matrix and embeded graphite crystals, primarily by the atomic diffusion with a ratchet mechanism and secondarily by the self-carburizing with gaseous carriers.

(6) The self-carburization induced from the growth behaviour of cast iron was applied to the surface-hardening of sintered iron with carbon in its cavities. The maximum hardness of the specimen was increased confirmedly to 700 Hv at the surface after the heating to 930°C for 30 min in 6% oxygen air and quenching.

(7) Low growth of cast iron with fine eutectic graphite flakes was attributed to the short ranges in carbon diffusion and the less penetrating of oxidation caused in heating to austenite temperature in air.

(8) Analytical computing was performed by a micro-computer for predicting imperfection in gray iron castings due to solidification shrinkage. Fractional volume of shrinkage cavity was com-

puted progressively on each element in a modeled casting during the solidification under simplified conditions. The computing needed about 18 hours to indicate a location of shrinkage cavity probable in the model. The result was checked experimentally by a commercial casting.

Oral Presentation

Hole Drilling Method on Casting Stress Analysis in Gray Iron Casting; T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture Meeting of Japan Foundrymen's Society, June 1984

Effect of Oxygen Concentration in Atmosphere on the Growth of Flake Cast Iron; M. Souma and K. Nagaoka: The 105th Grand Lecture Meeting of Japan Foundrymen's Society, May 1984

Effect of Graphite Phases on Growth of Cast Iron; K. Nagaoka: The 24th Committee (Cast Iron) of the Japan Society for the Promotion of Science, July 1984

Irreversible Carbon Diffusion in Growth of Cast Iron; K. Nagaoka and M. Souma: Third International Symposium on the Physical Metallurgy of Cast Iron (Stockholm), Aug. 1984

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

K. Ito, M. Taniguchi, S. Goto, K. Murasawa,
S. Ohno, H. Sato and Y. Sugita

Our laboratory is mainly concerned with studies on corrosion of metallic materials used in nuclear industries, characterization of iron rust and improvement of hydrogen reservoir alloys.

Research subjects in progress are summarized as follows:

(1) Corrosion of Hastelloy-N containing niobium was investigated in molten FLINAK salts with and without tellurium. The effect of tellurium on corrosion resistance was not apparent in the molten FLINAK salt without tellurium, but remarkable with tellurium. The results indicated the existence of an optimum niobium content in view of corrosion rate. Corrosion mechanisms was discussed in terms of in-depth profiles of the constituent elements, such as Nb, Cr, Mo, Ni and Fe.

(2) Corrosion study of SUS 304 and 316 was continued in organic and inorganic decontamination reagents for primary water-coolant circuits of nuclear reactors.

(3) Controlling parameters and mechanism were investigated on the formation of major components of iron rust. Special attention was referred to the condition to form superparamagnetic α-FeOOH and α-Fe_2O_3 in measuring the Néel temperature.

(4) Dissolution of synthesized Fe_3O_4 was investigated in decontamination reagents containing EDTA.

(5) Hydrogen uptake of nonstoichiometric Ti–Fe alloys was kinetically investigated by the pressure sweep method which was specially designed by our laboratory. Initial absorption properties

was improved by adding manganese in these hydrogen reservoir alloys.

Dr. T. Mizuno returned from the work with Prof. J. O'M. Bockris at the Texas A & M University in March, 1985.

Oral Presentation

Improvement of Initial Hydrogen-Absorption Characteristics and Structure Change by Making Composition of Iron-Titanium alloys Nonstoichiometric ; T. Mizuno and T. Morozumi : The Joint Fall Meeting of the Hokkaido Sections of Japan Institute of Metals and Iron and Steel Institute of Japan, Nov., 1983.

Behaviors of Nuclear Fuel Elements during Reactor Accidents ; H. Ohashi : The 1st Meeting of the Hokkaido Section of the Atomic Energy Society of Japan, Jan., 1984.

Corrosion of Reactor Materials Under the Coal Hydrogenation Reaction Condition ; T. Morozumi : The 21st Meeting of Hokkaido Coal Research Society : Symposium on the catalysts and Materials in Connection with Coal, Aug., 1984.

The Effect of Surface Treatment and Substrate Metal on Electrochemical Behavior After Passivation in a Borate Buffer Containing 8-Hydroxyquinoline

Hidetaka Konno and Henry Leidheiser, Jr.

Proc. Intl. Symp. Fundamental Aspects of Corrosion
Protection by Surface Modification, The
Electrochem. Soc., 1984, p. 245

The anodic and cathodic behavior of iron, copper, and zinc was studied after a two-step anodization in a borate buffer to which 8-hydroxyquinoline was added prior to the second step. The effect of the method of surface preparation prior to anodizing and chromate post-treatment after anodizing was determined for steel. Surface analyses were performed on the chromated samples. (English)

Selective Dissolution and Surface Enrichment of Binary Alloys

Masahiro Seo

Boshoku Gijutsu, **33,** No. 3, 162 (1984)

This review deals with selective dissolution and surface enrichment of binary alloys subjected to anodic polarization in aqueous solution. The theoretical and experimental aspects of selective dissolution were described on the basis of the volume diffusion mechanism. Furthermore, the corrosion resistivity of iron base alloys was discussed from the point of view of selective dissolution of iron component followed by chromium-enrichment in the vicinal alloy layer at the film/alloy interface. (Japanese)

Corrosion of Carbon Steel in High Temperature Water and the Structure of Surface Oxide Films

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

Proc. 9th LCMC Vol. 4, 235 p. (1984)

The corrosion behavior of carbon steel in high temperature water was examined as functions of 1) dissolved oxygen concentration (DO=50∼2500 ppb), 2) temperature (T=100∼250°C), and 3) corrosion time (t=1∼4 days). The structure and composition of the formed oxide was also examined by a) electron microscopy, b) X-ray diffraction, and c) X-ray photoelectron spectroscopy. The factors controlling the corrosion rate are discussed. (English)

Anodic Oxidation Behavior of Aluminum in 13 M and 1.5 M Sulfuric Acid Solutions

Yutaka Fukuda, Toshiro Fukushima
and Masaichi Nagayama

J. Metal Finishing Soc., **35**, 189 (1984)

Pure aluminum specimens were anodically oxidized in 13 M and 1.5 M sulfuric acid solutions at constant c. d. s and measurements were made of the amount of Al^{3+} ions accumulated in the formed oxide (W_f), the amount dissolved in the solution (W_d), and the coating ratio of the film. It was found that the sum of W_f and W_d was always equal to the total amount of oxidized aluminum (W_T) as calculated from the quantity of electricity. The amounts of W_f and W_d increased almost linearly with anodization time t_a. For any given value of W_T, the value of W_d obtained was smaller for the 13 M solution than for the 1.5 M solution, suggesting that the dissolution of the barrier layer at the pore-base proceeds more slowly in the 13 M solution than in the 1.5 M solution. This concept explains the high voltages and high current efficiencies observed for the formation of 13 M films. Since the 13 M films had smaller values of W_d and larger amounts of SO_4^{2-} ions compared to the 1.5 M films, their weights and coating ratios were always larger. In the case of the 13 M films, η and CR decrease appreciably with the lapse of anodizing time. This is due to the marked chemical dissolution of the pore during anodization. (English)

Interpretation of the Voltage-Current Characteristics Observed When Anodizing Aluminum in Acid Solutions

Ken Ebihara, Hideaki Takahashi
and Masaichi Nagayama

J. Metal Finishing Soc., Japan. **35,** 205 (1984)

An attempt is made to explain steady voltage-log current (E_a-log i_a) curves obtained for the anodization of aluminum in acid solutions, by applying a theory so far reported for high-field ion conduction in crystalline solids. The theory is modified to some extent by taking into account two factors : the semi-spherical shell structure of the barrier layer by which the applied voltage is sustained, and the formation and repair of defects in the barrier layer which are appreciable at higher voltages. The interpretation of E_a-log i_a behavior, including the effect of temperature, is quite satisfactory. (English)

Surface Segregation of Molybdenum During Pitting Corrosion of a Nickel-Molybdenum Alloy

M. Moriya and M. B. Ives

Corrosion **40**, 105 (1984)

Thin film samples of single-phase nickel-13 Wt% molybdenum alloy have been subjected to a localized pitting attack in chloride-containing solution. On subsequent analysis by scanning transmission electron microscopy using a variety of examination modes, it is observed that crystallographic pits are formed in the foil and that a molybdenum rich phase accumulates preferentially within the pits. The levels of chloride concentration on the pitted sample surface are below those detectable by the instrument. (English)

Examinations on the Properties of Experimentally Produced Hastelloy N

K. Sugiyama, R. Ishiguro, M. Moriya
and T. Morozumi

Research on Thorium Fuel (Reports of Special Project
Research on Energy Under Grant in Aid of
Scientific Reaearch of the Ministry of
Education, Science and Culture
Japan), 193 (1984)

An experimental study was conducted to clarify the tensile properties and the corrosion behaviours of experimentally produced Hastelloy N. The tensile properties were measured at temperatures of from ambient to 800°C. The results were favorably compared with those reported by ORNL. The corrosion test was made at 800°C using Flinak. The electron probe mass analysis and the scanning electron microscope were used for chemical analysis and metallographic examination. It was confirmed that the corrosion properties of the present material are comparable to those of the standard Hastelloy N produced by the Cabot Corporation, USA. (English)

Protection of 60/40 Brass from Dezincification by Corrosion Inhibitors

Takenori Notoya and Tatsuo Ishikawa

Bulletin of the Faculty of Engineering,
Hokkaido University, No. 117,
p. 11 (1984)

Five different types of copper or zinc complexing agents as dezincification inhibitors for 60/40 brass were tested using a potentiostatic acceleration technique in 0.5 M NaCl solution containing an acetic acid-sodium acetate buffer solution of pH 4.43. The potential of 60/40 brass electrode was maintained for 3 hours at a potential -200 mV vs. S. C. E. which was 100∼150 mV higher than the corrosion potential in the solution at 60°C. Benzotriazole (BTA) and tolyltriazole (TTA) were found to be effective inhibitor not only in preventing anodic dissolution of both copper and zinc but also in controlling the growth rate of dezincification layer in the 60/40 brass. 2.5-dimercaptothiadiazole (DMTDA) and 2-mercaptobenzothiazole (MBT) are effective inhibitors for the anodic dissolution but they are not as effective as BTA and TTA in the process of dezincification layer formation. Phytic acid (PA) shows an acceleration of 60/40 brass corrosion. The inhibition mechanism of these four inhibitors is probably due to the formation of copper and/or zinc complex films on the metal surface. It is concluded that an addition of the most promising inhibitors such as BTA and TTA to corrosive environments is an alternative method to prevent dezincification attack of 60/40 brass. (English)

Evaluation of Corrosion Inhibitors for Dezincification of 60/40 Brass

Takenori Notoya and Tatsuo Ishikawa

Proceedings of 9th International Congress on
Metallic Corrosion Vol. 1 p. 333 (1984)

Inhibition action of six different organic inhibitors for dezincification of 60/40 brass was evaluated under potentiostatic conditions by solution analysis of dissolved copper and zinc, and by amount of electric charge after addition of inhibitor. The measurements were conducted in 0.5 M NaCl containing acetic acid buffer solution with pH 4.43 at 60°C. The inhibitors used include commercial inhibitors for either copper or zinc and chelating reagents for chemical analysis. Among six inhibitors 2-mercaptobenzimidazole, benzotriazole and tolyltriazole were found to be effective not only in inhibiting dissolution of copper and zinc but also in controlling the growth rate of dezincification layer in 60/40 brass. (English)

Inhibition of Dezincification in 60/40 Brass by Organic Inhibitors

T. Notoya

Journal of the Japan Copper and Brass Research
Association Vol. 23 p. 36 (1984)

Six different types of copper or zinc complexing agents as dezincification inhibitors for 60/40 brass were tested using a potentiostatic acceleration technique in 0.5 M NaCl solution containing an acetic acid-sodium acetate buffer solution of pH 4.43. The potential of 60/40 brass electrode was maintained for 3 hours at a potential -200 mV vs. S. C. E. which was 100~150 mV higher than the corrosion potential in the solution at 60°C. Inhibition action was eavluated by solution analysis of dissolved copper and zinc and by amount of electric charge after addition of inhibitor. Mercaptobenzimidazole (MBI), benzotriazole (BTA) and tolyltiazole (TTA) were found to be effective inhibitors not only in preventing anodic dissolution of both copper and zinc but also in controlling the growth rate of dezincification layer in the 60/40 brass. Dimercaptothiadiazole (DMTDA) and mercaptobenzothiazole (MBT) are effective inhibitors for the anodic dissolution but they are not as effective as MBI, BTA or TTA in the process of dezincification layer formation. The inhibition mechanism of these inhibitors is probably due to the formation of copper and/or zinc complex films on the metal surface. It is concluded that an addition of the most promising inhibitors such as BTA and TTA to corrosive environments is an alternative method to prevent dezincification attack of 60/40 brass. (Japanese)

Dezincification of Brasses

T. Notoya

Boshoku Gijutsu (Corrosion Engineering)
Vol. 33, No. 2, 121 (1984)

Dezincification phenomena in brasses are reviewed. Dezincification mechanisms include (i) selective dissolution of zinc, (ii) preferential dissolution of zinc followed by redeposition of copper and (iii) the combination of the two. Prevention techniques for dezincification attack are (i) addition of small amount of alloying element, (ii) heat treatment of the manufactured components and (iii) inhibitor application. Dezincification tests in use are also described. (Japanese)

Ion Selectivity and Electro-Osmose in Porous Precipitate Films of Hydrated Iron (III) Oxide

M. Sakashita, T.Shimakura and N. Sato

Proceedings 9th International Congress on Metallic
Corrosion, Vol. 1, p. 126 (1984), National
Research Council Canada

Ion selectivity and electro-osmotic flow in porous precipitate films of hydrated iron (III) oxide have been studied by measuring the membrane petential and volume flux. The ion selectivity of the films depends on the concentration of H^+ ions and on the valency of coexisting ions in electrolyte solutions. The films are anion selective in LiCl and KCl solutions more acidic than a critical pH defined as the point of iso-selectivity pH_{pJs}, and the electro-osmotic flow takes place in the direction of chloride ion transport. The mole ratio of transfering water to transfering chloride ion determines the maximum chloride concentration in an inner solution between the porous film and the metal substrate. It is shown that the ion selective and electro-osmotic property of precipitate films plays a significant role in the corrosion of metals. (English)

Adsorption of Zn^{2+} Ions on MnO_2

Hiroki Tamura and Masaichi Nagayama

Progress in Batteries and Solar Cells, 5, 143 (1984)

For the characterization of MnO_2 samples (International Common Samples No. 1 and No. 8), the behavior of Zn^{2+} ion adsorption was examined as a function of pH and the equilibrium concentration of Zn^{2+} ions in solution, $[Zn^{2+}]$. The adsorption density Γ, or the amount of adsorbed Zn^{2+} on MnO_2 per unit area, increased with increasing pH and $[Zn^{2+}]$. The surface of MnO_2 in aqueous solutions is considered to be covered with amphoteric hydroxyl groups ($\equiv MnOH$); it releases a H^+ ion as an acid to become a negative site ($\equiv MnO^-$) and it receives a proton as a base to become a positive site ($\equiv MnOH_2^+$) depending upon pH. The amounts of neutral and charged sites were determined as a function pH by acid-base titrations. The adsorption of Zn^{2+} ions on MnO_2 was assumed to occur by exchanging m numbers of protons in the hydroxyl groups with a Zn^{2+} ion to form a surface complex:

$$Zn^{2+} + m \equiv MnOH \rightleftharpoons (\equiv MnO)_m Zn^{2-m} + mH^+ \tag{1}$$

The equilibrium constant K_m of this reaction is derived as:

$$\begin{aligned} K_m &= \frac{[(\equiv MnO)_m Zn^{2-m}]\,[H^+]^m}{[Zn^{2+}]\,[\equiv MnOH]^m} \exp(A[(\equiv MnO)_m Zn^{2-m}]) \\ &= \frac{\Gamma \cdot [H^+]^m}{[Zn^{2+}]\,([\equiv MnOH]_{\Gamma=0} - m \cdot \Gamma)^m} \exp(A \cdot \Gamma) \end{aligned} \tag{2}$$

where $[\equiv MnOH]_{\Gamma=0}$ is the surface density of unadsorbed sites, and A is a constant. The exponential term is derived by considering that the chemical potential of adsorbed Zn^{2+} ions increases linearly with Γ causing retardation of adsorption. The values of the constants K_m, m and A are determined by non-linear regression analysis of the experimental data of $[H^+]$, $[Zn^{2+}]$, Γ and $[\equiv MnOH]_{\Gamma=0}$ using eq, (2). It is clear that the different properties of respective samples are reflected in the values of the constants. (English)

The Composition and Properties of a Protective Layer Formed on a Steel by Anodizing with 8-Hydroxyquinoline

Hidetaka Konno, Masaichi Nagayama,
Henry Leidheiser, Jr.
and Richard D. Granata

J. Metal Finish. Soc. Japan, **35,** No. 8, 402 (1984)

Carbon steel specimens were anodized by a two step procedure, first in a borate solution and second in a borate solution containing 8-hydroxyquinoline [HQ]. The resulting surface inhibits cathodic reactions such as oxygen reduction and hydrogen evolution, and it has good corrosion resistance in aerated chloride media of pH 3∼10. The composition and structure of the formed layer were analysed by UV-VIS-IR reflectance spectroscopy, Auger electron spectroscopy combined with argon ion sputtering, conversion electron Mössbauer spectroscopy, and ellipsometry. The results indicate that the protective layer is composed of two layers: the outer layer is less than 40 nm in thickness and consists of condensation products of HQ and HQ derivatives formed by the anodic polarization, and the inner layer is less than 3 nm in thickness and consists of Fe-HQ and/or-HQ derivatives complexes. Electrochemical measurements revealed that the inner Fe complex layer is responsible for the corrosion protection in aerated chloride media. (Japanese)

Quantitative Analysis of Depth-Composition Profiles of Surface Oxide Films on Steel

Masahiro Seo and Norio Sato

Transactions ISIJ, 24, 669 (1984)

Auger electron spectroscopy (AES) combined with sputter-etching technique has been used for depth-composition analysis of very thin oxide films (1～100 nm) formed on steel surfaces. This review deals with various problems of the sputter-etching such as sputtering yield, selective sputtering and knock-on effect for quantitative depth-analysis of thin oxide films. Furthermore, discussions are made on the factors influencing the depth-resolution of the oxide film/metal interface. (English)

Potential-pH Diagram of Composition/Structure of Passive Film on Iron

R. Nishimura and N. Sato

Proceedings 9th International Congress on Metallic
Corrosion, Vol. 1, p. 96 (1984), National
Research Council Canada

The composition, layer structure and thickness of the passive films formed on iron in borate and phosphate solutions have been examined as functions of pH, potential and film formation procedure (one-step and two-step oxidation) by means of cathodic reduction combined with ellipsometry and chemical analysis. It is found that these properties of passive films are related to all of the variables investigated. The results are explained in terms of the ion selective property of the passive film, and the layer structure and composition are summarized in the potential-pH diagram. (English)

Spectra of the Thin Surface Oxide Films Anodically Formed on Iron and Titanium

T. Ohtsuka, K. Azumi and N. Sato

Proceedings the 13th Congress of the Intern. Commision for
Optics, Ed. by H. Ohzu, The Organizing Committer
of ICO-13, Sapporo, 554 (1984)

The spectrum of complex refractive index of anodic oxide films on iron and titanium was measured by 3 parameter reflectometry in order to investigate the semiconductive property. The anodic oxide film on iron exhibits a resemblant absorption spectrum to that of α-Fe_2O which includes two adsorption edges for photo excitation of the band electron. The anodic oxide film on titanium has a absorption edge at $h\nu = 3.2$ eV, whose photon energy is slightly larger than the band gap (3.05 eV) of bulk TiO_2. This discrepancy may be attribated to the hydration effect of the anodic oxide film.
(English)

Raman Spectroscopy Applied to the Oxide Films Formed on Metals in Air and in Aqueous Solution

T. Ohtsuka, N. Goto and N. Sato

Proceedings IXth International Conference on
Raman Spectroscopy, The Chem. Soc.
Japan, Tokyo, 456 (1984)

The oxide films thermally formed on SUS 304 stainless steel in air and anodically formed on titanium in aqueous solution were studied by laser Raman spectroscopy. The oxide film on the stainless steel was found to change in its composition at a temparature of 700°C. Below 700°C the main compounds of the film are α-Fe_2O_3 and Fe–Cr spinel oxide and above 700°C however the main compounds turn to Fe–Cr spinel oxide and Cr_2O_3. For the anodic oxide film on titanium the anatase type of TiO_2 was identified in the potentiostatic oxidation at 10.6 V vs RHE in pH 6.9 phosphate solution. (English)

An Auger Study of Selective Surface Oxidation of Ni-Cr Alloys

Masahiro Seo and Norio Sato

Proceedings 9th International Congress on Metallic
Corrosion, Vol. 2, p. 362 (1984), National
Research Council Canada

A series of Ni-Cr alloy specimens were oxidized for 1 h at 693~823 K in pure oxygen at a pressure of 1.33×10^4 Pa. The depth-profiling of oxidized surfaces, performed with simultaneous use of Auger electron spectroscopy (AES) and argon-ion sputter-etching technique, reveals that the Cr component is selectively oxidized and that a Cr-depletion zone is formed in the underlying alloy. The thickness of the Cr depletion zone depends on the bulk alloy composition and increases with increasing oxidation temperature. The values of the interdiffusion coefficient of underlying alloy, estimated from the Cr depletion profile by taking the composition broadening at the film/alloy interface due to sputter-etching into account, are two or three orders of manitude as large as the values extrapolated from the lattice diffusion data of the corresponding alloy obtained at elevated temperature. (English)

The Structure of Anodic Films Formed on Nickel and Nickel-13 w/o Molybdenum Alloy in pH 2.8 Sodium Sulfate Solution

M. Moriya and M. B. Ives

Corrosion **40,** 62 (1984)

Anodized thin film samples of single phase nickel 13 w/o (weight percent) molybdenum have been analyzed by scanning transmission electron microscopy using a variety of examination modes. It is established that the anodic film comprises a fine mosaic of almost epitaxial crystalline nickel oxide particles of 3 nm diameter. Characteristic X-ray analysis suggests that molybdenum is concentrated in the surface of anodized samples, but there is no electron diffraction evidence for a crystalline molybdenum oxide. It is suggested that molybdenum is present in the anodic film as either a finely dispersed or an amorphous oxide or as a hydrated phase. A model of the anodized films leads to an explanation of the effects of molybdenum alloying additions on the electrochemical characteristics of single phase nickel-molybdenum alloys. (English)

The Application of Scanning Transmission Electron Microscopy (STEM) to the Study of Thin Anodic Films on Nickel and Nickel-Molybdenum Alloys

M. Moriya and M. B. Ives

J. Microscopy, **133**, Pt 2, 155–170 (1984)

Anodized thin-film samples of nickel, molybdenum and a nickel-13 w/o molybdenum alloy have been analysed by scanning transmission electron microscopy, using selected area diffraction, micro-diffraction and X-ray micro-analysis.

Thin-film samples were obtained by ion thinning with argon and by electropolishing in acetic acid-perchloric acid. Electropolishing is the preferred technique for these studies, producing a surface with roughness on a scale of 1 nm.

The anodized films on nickel and nickel 13 w/o molybdenum alloy exhibit a rugosity with a 'particle' size of 3 nm. The crystal structure of the films is similar to f. c. c. nickel oxide.

Molybdenum enrichment was detected in the anodized alloy surfaces but there is no electron diffraction evidence for a crystalline molybdenum oxide. The electron diffraction pattern from anodized pure molybdenum suggests that the surface film is amorphous. (English)

The Structure of Passive Films on Single-Phase Nickel-Molybdenum Alloys

M. B. Ives, V. Mitrovic-Scepanovic
and M. Moriya

Proc. 5th Intern. Symp. on Passivity, 325–331 (1983)

The effect of molybdenum alloying additions on the structure and properties of passive films formed on nickel in acid sulphate solution has been studied by a combination of electrochemical measurements and physical surface analytical techniques. In particular, scanning transmission electron microscopy has been possible on anodized thin films of the alloys. Molybdenum is detected on the anodized surfaces after removal from solution, but both its distribution in the films and its presence in a crystalline phase has not been resolved. (English)

Distribution of Anions and Protons in Oxide Films Formed Anodically on Aluminum in a Phosphate Solution

H. Takahashi, K. Fujimoto, H. Konno
and M. Nagayama

J. Electrochem. Soc., **131,** 1856 (1984)

Pure Al foil specimens were galvanostatically anodized in a neutral phosphate solution (pH=7.0, 20°C), and the thickness and composition profile of the formed oxide films were examined as functions of the anode potential and current density (c. d.). Analysis of the films was made by chemical sectioning with a H_2SO_4 solution, combined with (i) electron microscopy, (ii) X-ray photoelectron spectroscopy, (iii) capacitance measurements, (iv) dc polarization measurements, and (v) solution analysis. The films were found to consist of two parts, an outer part containing PO_4^{3-} and OH^- ions, and an inner part consisting of pure alumina. The outer part dissolved in the H_2SO_4 solution at a rate faster than that of the inner part, and thus the two parts were clearly distinguished by following the time variations in the reciprocal of capacitance during the chemical sectioning. For films formed with a constant c. d., the thickness ratio of the two parts. δ_{out}/δ_{in}, and the phosphate concentration in the outer part do not change with the anode potential or the total film thickness. With increasing c. d., the two values tend to increase. The mechanism controlling the anion and proton distribution in the oxide film is discussed. (English)

Breakdown of Oxide Films on Aluminum in Neutral Solutions Containing Organic and Inorganic Anions

H. Takahashi, M. Mukai and M. Nagayama

Proc. of 9th ICMC Vol. 2 155 p. (1984)

Deterioration of anodic oxide films on aluminum during immersion in water with/without addition of anions has been followed by measuring a) the amount of dissolved Al^{3+} ions, b) film capacitance and c) anodic polarization behavior.

In solutions of adipate, borate, sulfate and chloride and in pure water as well, the hydration of oxide occurs predominantly while film dissolution is predominant in oxalate, citrate, and tartrate solutions. In phosphate solutions with low concentrations, neither dissolution nor hydration occurs and the film is completely stabilized. The films start to dissolve with the formation of hydrated layer, as the concentration is increased, and the dissolution is facilitated and the hydration is suppressed at higher phosphate concentrations and low pHs. (English)

Characterization of Solid Surface by Polarized-light Reflectometry

T. Ohtsuka

Shokubai (Catalyst), 26, 227 (1984)

Recent results on the study of solid surfaces by ellipsometry and reflectometry were summerized. 1) Princeple and apparatus. 2) Adsorption of gas on metals. 3) Adsorption of anion on metal electrodes. 4) Anodic oxide films on metal electrodes. 5) Application to the metal deposition process. 6) Estimation of semiconductor surface. 7) Spectroscopic measurements. 8) Microscopic ellipsometry. (Japanese)

Sulfidation Properties of an Fe-26.6 at.% Cr Alloy at Temperatures of 973-1173 K in H_2S-H_2 Atmospheres at Sulfur Pressures 10^4-10^{-6} Pa

T. Narita and W. W. Smeltzer

Oxidation of Metals, Vol. 21,
Nos. 1/2, 39 (1984)

An investigation is reported on the sulfidation properties of an Fe-26.6 at.% Cr alloy at 973, 1073, and 1173 K in H_2S-H_2 atmospheres at sulfur pressures $10^4 \geqslant P_{S_2} \geqslant 10^{-6}$ Pa. The sulfidation kinetics when plotted according to a parabolic relationship usually exhibited an early slow transient period before onset of parabolic kinetics. Scales contained up to three layers. A triplex $(CrFe)S_x$/$(CrFe)_3S_4$/-$(FeCr)S_x$ scale was formed at high sulfur pressures (range I), a single-phase $(FeCr)S_x$ or a duplex $(CrFe)S_x$/(FeCr)S scale at intermediate sulfur pressures (range II), and a single-phase $(CrFe)S_x$ scale at low sulfur pressures (range III). These pressure ranges at 973 K were: range $I \geqslant P_{S_2} = 10^{-2}$ Pa, $10^{-2} > P_{S_2}$ (range II) $\geqslant 10^{-5}$ Pa, and range $III < P_{S_2} = 10^{-5}$ Pa. The initial lower and upper pressures shifted to higher values at increasing temperature, becoming 10^{-4} and 10^1 Pa at 1073 K, and 10^{-3} and 10^2 Pa at 1173 K. $(CrFe)_3S_4$ was the slow growing phase, and (FeCr)S was the most rapid growing phase in the scales. Copious internal sulfidation precipitates occurred in the alloy beneath a $(CrFe)S_x$ scale at 1173 K, but the precipitates were confined to the alloy grain boundaries beneath this scale at 1073 and 973 K. Different methods of surface preparation and preoxidation of the alloy to yield thin $(CrFe)_3O_4$ and $(CrFe)_2O_3$ films did not effectively retard the sulfidation kinetics. (English)

Sulfidation Mechanism of an Fe-26.6 at.% Cr Alloy at Temperatures 973-1173 K in H_2S-H_2 Atmospheres at Sulfur Pressures 10^4-10^{-6} Pa

T. Narita and W. W. Smeltzer

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An investigation has been carried out to establish the sulfidation mechanism of an Fe-26.6 at.% Cr alloy at 973, 1073, and 1173 K in H_2S-H_2 atmospheres at sulfur pressures $10^4 \geq P_{S_2} \geq 10^{-6}$ Pa. Electron microprobe analyses were made for the distribution of chromium, iron, and sulfur across the scales and in the alloy substrate. The structural properties of the sulfide phases in the scales and of several sulfides equilibrated with H_2S-H_2 atmospheres were determined by X-ray techniques. Platinum wire marker measurements were carried out to determine the migrating species in the scales. These experimental results confirm that a triplex $(CrFe)S_x \backslash (CrFe)_3S_4 \backslash (FeCr)S_x$ scale is formed at high sulfur pressures, a single-phase $(FeCr)S_x$ or duplex $(CrFe)S_x \backslash (FeCr)S_x$ scale at an intermediate sulfur pressure range, and a single-phase $(CrFe)S_x$ scale at low sulfur pressures. The sulfide layers in the scales grow by predominant diffusion of metal except for the very thin innermost porous $(CrFe)S_x$ layer in triplex scales, which involves sulfur ingress. (English)

Sulfidation Properties of an Fe-23.4Cr-18.6Al Alloy at Temperatures 1073 and 1173 K in H_2S-H_2 Atmospheres of Sulfur at Pressures 10^4-10^{-5} Pa

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

Oxidation of Metals, Vol. 22,
Nos. 3/4, 181 (1984)

An investigation is reported on the sulfidation properties of an Fe-23.4Cr-18.6Al(at.%) alloy at 1073 and 1173 K in H_2S-H_2 atmospheres, $10^4 > P_{S_2} \geq 10^{-5}$ Pa. The sulfidation kinetics exhibited an early transient period before onset of parabolic kinetics. Values of the parabolic sulfidation rate constants increased by as much as 10^5 from their smallest values at low sulfur pressures, $P_{S_2} \leq 10^{-4}$ Pa, to maximum values at sulfur pressures $P_{S_2} \sim 10^2$ Pa. Multilayered scales were formed, the number and types of layers dependent on sulfur pressure. A fully developed scale at sulfur pressures $P_{S_2} > 10^{-3}$ Pa was composed of three layers; the inner and intermediate layers contained several quaternary sulfides, hexagonal $(AlCrFe)_2S_3$ and $(FeCr)Al_2S_4$, and spinels $(FeAl)Cr_2S_4$ and $(CeFe)Al_2S_4$, whereas the outer porous layer of isolated needles and plates was composed of FeS. This ternary alloy is shown to exhibit more superior sulfidation resistance than a binary Fe-26.6 Cr alloy. (English)

Effect of Oxygen Concentration in Atmosphere on the Growth of Falke Graphite Cast Iron in Austenite Region

M. Souma and K. Nagaoka

IMONO 56, 5, 269-275 (1984)

In order to elucidate the role of oxygen in promoting the growth of flake graphite cast iron in austenite region, growth tests were carried out on as-cast and pre-grown irons in air of various oxygen concentration. (1) Growth was remarkable in the dilute oxygen air and saturated at higher than 10% oxygen. (2) The growth promotion due to oxygen was increased in the pre-grown iron where the growth in 2% oxygen air was 3.6 times that in 0% oxygen, while the figure was 2.9 in the as-cast iron. (3) The weight of irons decreased by heating in the 2% oxygen air while appreciable growth occurred. On the other hand, the growth saturated in more than 10% oxygen air, in spite of the weight increase. (4) Pearlitic zone developed remarkably below the decarburized surface zone, especially in the pre-grown iron and in the high oxygen range. (5) Growth-promotion in dilute oxygen atmosphere is explained theoretically by a hypothesis of self-carburization due to an atmosphere internally caused by the reaction of graphite and oxygen. Internal carburization may increase nominal expansion and redistribution of graphite during heating and cooling, and may promote growth consequently. (6) Complicated effect of oxygen on growth in medium oxygen concentration may depend on the oxygen permeability of oxidized surface zone in cast iron. (Japanese)

Fracture Toughness Evaluation of Flake Graphite Cast Iron by R-Curve Method

T. Noguchi, T. Terada and K. Nagaoka

IMONO, 56, 9, 553-558 (1984)

In order to evaluate fracture toughness of flake cast iron, J_{Ic} test was performed on standard three point bending specimens of FC 15~30 class irons and the implication of the obtained J_{in} value was discussed based on the $J-\Delta a$ curves and fracture process observations. The compliance method was used to estimate crack length as these are difficult to measure by standard methods.

The $J-\Delta a$ curves obtained indicate crack extention. Microscopic cracks initiate along graphite flakes around the notch tip and easily propagates. From these initial cracks, a macroscopic fracture propagates through the metallic matrix. This occurs at the nodal point in the $J-\Delta a$ curve. At the nodal point, the load is about 95% of the maximum load and the initial cracks have grown to 0.5~1 mm. The J_{in} defined by the nodal point was 0.5~1.2 kgf/mm for FC 15~30 irons, which gives a K_c value of 75~125 kgf/mm$^{2/3}$. This value is higher than the value calculated directly from the maximum load. Considering the ease of estimating, good experimental correlation with $K(J_{in})$, and its accuracy on the whole in application, $K(P_{max})$ can be adopted as a safe value for practical purpose although its mechanical implications are not clear. (Japanese)

Notch Strength of Sintered Steel

T. Noguchi

Journal of the Society of Materials Science,
Japan, 33, 371, 999-1005 (1984)

Notch characteristics in static strength of sintered steel was investigated experimentally and theoretically.

Circumferentially notched bars and edge notched plate specimens with various root radii were examined at room and liquid nitrogen temperatures. The fracture criterion was discussed based on the stress distributions calculated by the finite element method considering the nonelasticity of the material.

Sintered steel showed very low notch sensitivity at room temperature. Strength decrease by a notch was within 20% when the form factor was up to 3. At liquid nitrogen temperature it showed higher sensitivity, the strength decrease reached to about 50% for the same shape.

It was revealed that the low notch sensitivity was caused by the following two factors, same as in cast iron : the non-elasticity of the material that reduces the maximum working stress, and the existence of an over stressed region at the notch root where the stress is higher than the tensile strength. The over stressed depth at fracture was 1～3 mm at room temperature and 0.2～0.5 mm at liquid nitrogen temperature.

The smallest value of the over stressed depth which is several times the particle size is the minimum dimension of sintered steel treatable as a continuum solid. The large value is infered to be the propagating condition of an initiated cracks. (Japanese)

Stiffness and Strength of Castings — (1)

T. Noguchi

Bulletin of the Hokkaido Branch of the Japan
Foundrymen's Society, 71, 15-20 (1984)

In order to supply high quality castings of gray cast iron, it is very important to consider the design of configuration not only for metallurgical soundness but also for high strength/weight ratio especially in bending. Since gray cast iron behaves inelastically, usual elastic design formulas would cause large error in the calculation for strength of castings. Therefore the strength of gray iron castings must be evaluated adequately according to the method based on the mechanical characteristics of this material. Contents: 1) Introduction 2) Strength and Stiffness 3) Scale of stiffness in bending, I (moment of inertia) 4) Scale of strength in bending, Z (section modulus). To be continued. (Japanese)

Stiffness and Strength of Castings — (2)

T. Noguchi

Bulletin of the Hokkaido Branch of the Japan
Foundrymen's Society, 73, 19-23 (1984)

Continued from the previous paper. Contents : 5) Increase of I and Z 6) Plates 7) Other methods of increasing strength and stiffness 8) Conclusions. (Japanese)

Experimental Investigation of the Components of Network Model at Bipolar Disk Electrode with Many Holes

Takeshi Sasaki and Tatsuo Ishikawa

DENKI KAGAKU, **52**, 6 (1984)

The applicability of the network model to describing a bipolar electrode system has been investigated by the use of the disk electrode with many holes as the by-pass parts in acidic bichromate solutions. A method of determining the Faradaic current through bipolar electrodes as packed compactly in the cell is also described. The by-pass resistance which was determined by the unit cell voltage at one bipolar electrode, the Faradaic current and the by-pass current increased with the applied current. The increase is probably due to the variation in the pattern of current flow lines in the vicinity of the electrode holes, which is leads to the reduction in the electrolyte region for the by-pass current. It is concluded that the network model of the bipolar electrode system must be modified as expressing the by pass part by a variable resistance. (English)

Determination of Faradaic Current through a Bipolar Electrode in Acidic Bichromate

Takeshi Sasaki and Tatsuo Ishikawa

Bulletin of the Faculty of Eng. Hokkaido Univ.,
123, 15 (1984)

In order to elucidate the factors determining the proportion of the Faradaic current to the applied one, the Faradaic current through a bipolar electrode was measured under various conditions in acidic bichromate solutions.

A modified electrode was adopted for measurement of the Faradaic current in a compactly packed cell. The bipolar electrodes consisted of graphite disks with many drilled holes. The by-pass resistance, the electric resistance of the electrolyte filling the holes, widely varied with functions of the diameter and the number of the holes and the thickness of the electrodes. The interelectrode gaps were also varied.

The proportion of the Faradaic current to the applied one was substantially determined by the by-pass resistance independent of the daimeter and the number of holes, and the thickness of the electrode. As continuous electrolysis was carried out in the acidic bichromate solutions, the proportion of the Faradaic current remarkably decreased in low concentrations of Cr (VI) and this was responsible for the decrease in the gross current efficiency in the bipolar electrode cell. (English)

Pulverizing and Its Prevention of Hydrogen-storage Iron-titanium Alloy

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and T. Tabuchi

Bull. Faculty of Engineering, Hokkaido Univ.,
No. 122, 61 (1984)

A study was presented on the pulverizing behaviors of non-stoichiometric irontitanium alloy, in which hydrogen was repeatedly absorbed and desorbed. The characterization was made as a function of absorption-desorption cycle by measuring various physical and chemical properties : the hydrogen absorption rate and isotherm, the BET area, the particle size distribution, the X-ray diffraction and the Mössbauer spectrum. From the results of these measurements, it was concluded that major changes occurred in microstructures of alloy within fifty cycles of the initial absorption and desorption of hydrogen. Scanning electron-microscopic observation revealed, however, a delayed fragmentation due to the bond remaining on the tips of cleavages in alloy particles. Zinc coating was not quite inhibitive for the destruction of microstructure, but it effectively prevented the fragmentation. The effect was explained by assuming a capsulation of pulverized alloy with an envelope of zinc film. (Japanese)