ANNUAL REPORT

1978

CORROSION RESEARCH

Materials Science and Engineering

published
by
THE CORROSION RESEARCH GROUP

FACULTY OF ENGINEERING
HOKKAIDO UNIVERSITY

NO. 7 DECEMBER 1978

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

Professor N. Sato, Electrochemistry Laboratory,
Professor T. Ishikawa, Electrometallurgy Laboratory,
Professor T. Morozumi, Nuclear Reactor Materials Laboratory.

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

CONTENTS

page

Current Activities and Oral Presentations :

Abstract

Metal Physics :

Pitting Corrosion :

Corrosion, Anodic Oxidation and Passivity :

Corrosion Inhibitor :

Reactivity of Metal Oxide and Hydroxide :

Surface Analysis :

High Temperature Oxidation :

Chemistry of Hydrogen and Sulfur :

Analysis of Water :

ELECTROCHEMISTRY LABORATORY

Prof. Dr. N. Sato, Assist. Prof. Dr. M. Seo,
Dr. M. Sakashita, Dr. T. Ohtsuka
and Miss C. Miura.

Students

I. Iwata, N. Sato, H. Gotoh, H. Murayama, S. Fujita,
Y. Matsumura, N. Setoh and Y. Sera

Main subjects of research in this laboratory are concerned with surface electrochemistry of metals and alloys. The anion effect on anodic dissolution and passivation of iron and nickel is being continuously investigated by use of rotating ring-disc electrodes. Also, detailed information of the structure and composition of anodic oxide films on molybdenum and copper has been collected by surface analytical techniques such as AES and XPS. In addition, a fresh study on anodic oxidation of lead in sulfuric acid solution is commenced from this year. Further, the temperature effect on the composition profiles in depth of the stainless steels passivated in sulfuric acid solution has been investigated by simultaneous use of AES and argon ion sputter-etching. Besides, hydrogen permeability of high tension steels in acetic acid-sodium acetate solution containing hydrogen sulfide has been electrochemically measured in connection with hydrogen embrittlement and stress corrosion cracking of steels.

Participation of laboratory staffs in international meetings is as follows: In May, Professor Sato participated in the First Japan-U. S. Joint Symposium on Light Water Reactors held in Shizuoka, Japan, and presented a review paper as an introductory remark to high temperature water corrosion of iron-base alloys. In July, Assist. Prof. Seo attended the International Conference on Solid Films and Surfaces held in Tokyo, Japan and presented a paper "Differential composition profiles in depth of thin anodic films on ironchromium alloys". In August, Dr. Nishimura moved to Chugoku Government Industrial Research Institute and Dr. Ohtsuka came back to this laboratory as a research associate from the Technische Universität Clausthal, West Germany. In October, Professor Sato was invited to the 7th International Conference on Metallic Corrosion held in Rio de Janeiro, Brazil to give a plenary lecture on "The recent progress in techniques for corrosion study" with an additional contributed paper of the depth profile of passive films on iron-base alloys. After the Conference, he visited Argentina and Peru with other Japanese scientists. In November, Professor Sato and Dr. Sakashita attended the 3rd Japane-USSR Seminar on Electrochemistry held in Kyoto, Japan to present a paper of the ion transport through lead sulfate films in lead-acid battery.

Three foreign scientists visited this laboratory: Drs. J. A. Lira-Olivares and J. A. Pryor (Universidad Simón Bolivar, Caracas, Venezuela) on 1–4 May, and Professor R. A. Rapp (Department of Metallurgical Enginerring, The Ohio State University, Columbus, Ohio, USA) on 8–12 December.

Oral Presentations

Auger Analysis of Anodic Oxide Films on Molybdenum; N. Sato, R. Nishimura, M. Seo and N. Sato: The Annual Meeting of the Japan Electrochemical Society in Hokkaido, Jan., 1978.

The Effect of Multivalent Ions on Selective Ion Permeability of Precipitated Hydrous Iron Oxide (II, III) Membranes; Y. Yomura, M. Sakashita and N. Sato: *ibid.*, Jan., 1978.

Surface Polishing and Surface Composition of Fe–Cr Alloys; M. Seo and N. Sato: The Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1978.

Ionic Rectification and Corrosion Inhibition of Bipolar Precipitated Membrane; M. Sakashita and N. Sato: *ibid.*, Jan., 1978.

Potential-pH Diagram for Anodic Oxide Films on Iron; R. Nishimura and N. Sato: The Spring Meeting of the Japan Institute of Metals, Apr., 1978.

Differential Composition Profiles in Depth of Passive Films on Fe-

Cr Alloys ; M. Seo, T. Yui and N. Sato : The Spring Meeting of the Japan Society of Corrosion Engineering, May, 1978.

Ion Transport of Bipolar Precipitated Membrane ; M. Sakashita and N. Sato : *ibid.*, May, 1978.

Auger Analysis of Passive Films on Inconel 600 and Incoloy 800 Alloys ; M. Seo and N. Sato : *ibid.*, May, 1978.

Introductory Remark to High Temperature Water Corrosion of Iron-Base Alloys ; N. Sato : The First Japan-U. S. Joint Symposium on Light Water Reactors, Shizuoka, Japan, May, 1978.

AES and XPS Analysis of Anodic Oxide Films on Molybdenum ; N. Sato, R. Nishimura, M. Seo and N. Sato : The Hokkaido Section Meeting of the Japan Institute of Metals, June, 1978.

Anodic Oxidation of Copper in Neutral and Alkaline Solutions ; T. Iwata, R. Nishimura and N. Sato : *ibid.*, June, 1978.

Ellipsometric Spectorscopy and Differential Auger Analysis of Chromate Films on Iron ; H. Gotoh, M. Seo and N. Sato : *ibid.*, June, 1978.

Hydrogen Penetration in Steels ; N. Sato : The Hokkaido Section Seminar of the Japan Institute of Metals, June, 1978.

Pre-treatment and Surface Composition of 304 and 316 Stainless Steels ; M. Seo and N. Sato : The 19th Symposium on Corrosion and Protection of the Japan Society of Corrosion Engineering, July, 1978.

Differential Composition Profiles in Depth of Thin Anodic Oxide Films on Iron-Chromium Alloys ; M. Seo and N. Sato : The International Conference on Solid Films and Surfaces, Tokyo, Japan, July, 1978.

Polarization Characteristics of Lead Sulfate Membrane ; S. Fujita, M. Sakashita and N. Sato : The Summer Meeting of the Japan Chemical Society in Hokkaido, Aug., 1978.

Polarization Characteristics of Iron and Steels in Weakly Acidic Solutions Containing Hydrogen Sulfide : H. Murayama, M. Sakashita and N. Sato : *ibid.*, Aug., 1978.

Recent Progress in Techniques for Corrosion Study ; N. Sato : The 7th International Conference on Metallic Corrosion, Rio de Janeiro, Brazil, Oct., 1978.

Depth Profile of Passive Films on Iron-Base Alloys; M. Seo and N. Sato: *ibid.*, Oct., 1978.

Exo-electron Emission from Metal Surfaces during Catalytic Oxidation Reaction; M. Seo and N. Sato: The First Research Meeting of Exo-electron Emission and Its Application. Oct., 1987.

Passive Films on Iron-Group Metals and Their Formation; N. Sato: The 21st Symposium on Corrosion and Protection of the Japan Society of Corrosion Engineering, Nov., 1978.

Ion Selective Permeability of Corrosion Product and Passivation; M. Sakashita: *ibid.*, Nov., 1978.

Ion Transport through Lead Sulfate Film in Lead-Acid Battery; M. Sakashita and N. Sato: The 3rd Japan-USSR Seminar on Electrochemistry, Kyoto, Japan, Nov., 1978.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayma, Lecturer Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno, Mr. S. Emi,
Mr. N. Kamada Mr. Y. Otake
and Miss. M. Hachiro

Students

M. Koda, M. Oshima, K. Go, M. Kawai, Y. Ikawa (Miss)
S. Kobayashi, K. Fujimoto, T. Hozumi,
Y. Horii, and H. Ono.

Our laboratory has been interested in the problems related to anodic oxidation of metals, cathodic deposition of metals, X-ray photoelectron spectroscopy of metal surfaces and chemistry of metallic ions in aqueous solutions. Prof. Nagayama attended the Seattle Meeting of the Electrochemical Society (May, 1978) and the U. S.-Japan Joint Symposium on Corrosion Problems in Light Water Reactors (Fuji City, May-June, 1978). He was invited the Taiwan to give lectures at the Taiwan Normal University and the Tatung Institute of Techology (Taipei, Oct. 1978). Dr. Takahashi is on Leave to the U. S. A. to work with Prof. Yeager at the Case Western Reserve University, Cleveland. Research being conducted in our laboratory is as follows:

(1) The distribution of electrolyte anions in anodic oxide films formed on Al in neutral solutions.

'Barrier type' oxide films are formed in phosphate and borate solutions and the concentration profiles of the anions in the depth direction are examined as a function of the solution pH and anodizing time. Wa have adopted a technique of stripping films with a H_2SO_4 solution combined with chemical analysis of the solution, or XPS analysis of the oxide surface.

(2) Determination of the porosity of anodic oxide fimls on Al formed in acid electrolyte.

Aluminum specimens covered with porous anodic oxide are re-anodized in a neutral borate solution at a constant c. d. Oxide formation occurs simultaneously at the barrier layer/solution and the barrier layer/metal interfaces, corresponding to the migration of Al^{3+} and O^{2-} ions through the barrier layer. It is possible to estimate the porosity of the original porous oxide by analyzing the voltage-time curve measured in the re-anodization, and experiments are being conducted for films produced under various anodizing conditions. Changes in the structure of porous oxide during 'sealing' are also examined in this way.

(3) Effect of anion and Fe (III)-hydroxide on the air-oxidation of Fe^{2+} ions in neutral solutions.

Ferrous ions can be oxidized by the air to form Fe (III)-hydroxide in neutral solutions. In previous investigations, we found that some anions like HPO_4^{2-} and F^- accelerate the reaction and some like Cl^- and SO_4^{2-} retard it. The reaction product, Fe (III)-hydroxide, also facilitates the reaction. Attempts are being made to measure the rate of oxygenation in the presence of a large amount of Fe (III)-hydroxide together with particular anions.

(4) XPS studies on metal surfaces.

X-ray photoelectron spectroscopy has been applied to the investigate of the passive oxide films formed on iron in a neutral boric acid-borate solution. The passive oxide was composed of a hydrous Fe_2O_3 ($OH/Fe=0.3-0.5$) and some of the Fe ions had a valency higher than $+3$. The same technique is being used to examine the composition of chromic-chromate films formed on Pt during chromium plating with a conc. chromic acid solution containing sulfate. The surface of iron and stainless steels subjected to high temperature water with or without γ-ray irradiation has also been examined.

Oral Presentations

Dissolution behavior of Fe (III)-hydroxide in acid solution —Effects of Fe (III)-hydroxide preparation procedures ; H. Tamura, M. Oshima, and M. Nagayama : The 4th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1978.

XPS-analysis of passive oxide films formed anodically on Fe in a neutral boric acid-borate solution; H. Konno and M. Nagayama: *ibid.*, Jan. 1977.

Effect of pH on the formation behavior of Al anodic oxide films in phosphate solutions; H. Takahashi, T. Tamura and M. Nagayama: The 13th Annual Meeting of the Hokkaido Corrocion Research Association, Jan. 1978.

Acid dissolution behavior of Fe(III)-hydroxide prepared by hydrolyzing Fe(III)-sulfate; M. Oshima, H. Tamura and M. Nagayama: The 1978 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Jan. 1978.

Oxidative decomposition of chelating agents in laboratory waste water by chromic acid; S. Emi, N. Kameda, H. Tamura and M. Nagayama: *ibid.*, Jan. 1978.

Electrochemical properties of the barrier type oxide films on aluminum; H. Takahashi, T. Tamura and M. Nagayama: The 45th Annual Meeting of the Electrochem. Soc. of Japan, May, 1978.

Analysis of passive oxide films on iron by XPS; H. Konno and M. Nagayama, *ibid.*, May, 1978.

Adsorption of Zn^{2+} on Fe(III)-hydroxide; H. Tamura, K. Go and M. Nagayama: *ibid.*, May, 1978.

Analysis of solid surfaces by XPS; M. Nagayama and H. Konno: Seminar sponsored by the Hokkaido Section of the Japan Institute of Metals, April 1978.

The Mechanism of 'Pore-filling' of the porous oxide films on Al; H. Takahashi, M. Koda and M. Nagayama: The 153rd Electrochem. Soc. Meeting, Seattle, May 1978.

XPS analysis of chromic-chromate films formed by cathodic reduction of chromic acid solutions containing sulfate; H. Konno, M. Kawai and M. Nagayama: The 57th Meeting the Metal Finishing Soc. Japan, May 1978.

Composition and dissolution characteristics of anodic oxide films formed on Al in neutral phosphate solutions; H. Takahashi, T. Tamura and M. Nagayama: *ibid.*, May 1978.

Semi-quantitative analysis of anodic oxide films on Fe by XPS; H. Konno and M. Nagayama: The 39th Analytical Chemistry Symposium, June 1978.

Adsorption equilibria of Zn^{2+} ions on Fe(III) hydroxide; K. Go, H. Tamura and M. Nagayama: The 1978 Summer Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., Aug. 1978.

Anodizing of Al in acidic and neutral solutions; M. Nagayama: Seminar sponsored by the Metal Finishing Soc. of Taiwan, Taipei, Oct. 1978.

Mechanism of chromium plating reactions in chromic acid solutions containing sulfate; M. Nagayama: *ibid.*, Oct. 1978.

Mechanism of copper plating reactions in cupric pyrophosphate solutions; M. Nagayama: *ibid.*, Oct. 1978.

Determination of the porosity of porous anodic oxide films on Al by the pore-filling method; M. Nagayama: Lecture at the Chemistry Department, the National Taiwan Normal University, Taipei, Oct. 1978.

Electrochemical behavior and structure of anodic oxide films on Al formed in neutral borate solutions; M. Nagayama: Lecture at the Tatung Institute of Technology, Taipei, Oct. 1978.

Surface state of Fe(III)-hydroxide in neutal solutions; H. Tamura and M. Nagayama: The 58th Meeting of the Metal Finishing Soc. Japan, Nov. 1978.

Changes in the structure of porous anodic oxide films on Al by reaction with hot water; M. Koda and M. Nagayama: *ibid.*, Nov. 1978.

Oxidation treatment of chelating agents in waste water containing heavy metal ions; S. Emi, H. Tamura and M. Nagayama, *ibid.*, Nov. 1978.

Depth-profile of the anodic oxide films formed on Al in a neutral borate solution; H. Konno, S. Kobayashi and M. Nagayama, *ibid.*, Nov. 1978.

ELECTROMETALLURGY LABORATORY

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

Trust Researchers

Mr. M. Kawada and Mr. K. Sugita

Students

Z. Asano, S. Takeda, H. Metoki, S. Ohkubo, I. Kanaya
H. Suzuki, A. Naitoh and A. Fukuhara.

Research subjects in progress are as follows.

(1) Laboratory scale tests in single cells and 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. The electric conductivities of these molten salts and being measured in this temperature range for cell design and optimum operation of the cell.

(2) Concerning the electrolytic treatments of waste water from metallurgical processes, various bipolar cells are developed and various fundamental studies are also in progress.

(3) Studies on corrosion and inhibition mechanisms of copper and copper base alloys in chloride and sulfate solutions are being carried out using collector reagents used in copper oxide mineral processing operations from the viewpoint of examining the function of surface oxides on the metals in corrosion inhibitions processes.

(4) Immersion tests and resistometric test for corrosion of various metals are being undertaken in the low temperature molten salt system such as ammonium bisulfate melts at 200°C.

(5) In order to elucidate the effects of micro-vibration on corrosion of pipe-line materials, some fundamental corrosion tests are being started under controlled conditions of vibration.

Professor Ishikawa attended the 7th International Congress on Metallic Corrosion held in Rio de Janeiro, Brasil in October.

Oral Presentations

Reduction of Six Valent Chromium Ion in Various Types of Bipolar Electrode Cell; T. Sasaki, A. Kanazawa, and T. Ishikawa: 4th Hokkaido Section Meeting of Electrochemical Society of Japan, Jan., 1978.

Electrowinning of Solid Aluminum from Chloride Metls containing Aluminum Chloride; H. Tanda, S. Konda and T. Ishikawa: *ibid.*, Jan., 1978.

Analysis of Polarization Characteristics for Estimation on Cell Efficiency of Bipolar Electrode Cell; K. Sugita, M. Kawada and T. Ishikawa: *ibid.*, Jan., 1978.

Corrosion Inhibition of Al-4% Cu Alloy in Alkaline Solution; T. Notoya and T. Ishikawa: 13th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1978.

Corrosion Characteristics of Various Metals in Ammonium Bisulfate Melts; H. Metoki and T. Ishikawa: *ibid.*, Jan., 1978.

Corrosion Pretreatment for Copper-Zinc Alloys; G. W. Poling and T. Notoya: Annual Conference of NACE, Corrosion Research Conference in Houston, Texas, U. S. A., March, 1978.

Copper Corrosion Inhibition by 2.5-Dimercaptothiadiazole; T. Notoya and T. Ishikawa: 45th Annual Meeting of Electrochemical Society of Japan, April, 1978.

Electrowinning of Liquid Aluminum by using Funnel Pile Type Bipolar Electrode Cell (Part 5) Estimation of Working States by Transitional Polarization Behavior of the Electrolytic Cell; K. Sugita, S. Konda, T. Ishikawa, and M. Kawada: *ibid.*, April, 1978.

2.5-Dimercaptothiadiazol as a Corrosion Inhibitor for Copper and Copper Alloys; T. Notoya: '78 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1978.

Corrosion Behaviors of Various Metals in the Molten Salt of Ammonium Bisulfate; T. Ishikawa and H. Metoki: *ibid.*, May, 1978.

Operation of Funnel Pile Type Bipolar Cell; T. Ishikawa and M. Kawada: 13th Excutive Committee on Aluminum New Smelting Process, June, 1978.

Fundamental Studies on the Electrolysis of Aluminum Chloride; T. Ishikawa: 2nd Excutive Committee on Electrochemical Process, Committee of Fused Salt, Electrochemical Society of Japan, June, 1978.

Technical Problems on Bipolar Electrode Cell; T. Ishikawa: 3rd Round-table Conference on the Research of Electrolytic Engineering, July, 1978.

Copper Corrosion Inhibition with Insoluble Chelate Film Formation; T. Notoya and T. Ishikawa: The 1978 Summer Meeting of the Hokkaido Section of the Japan Chemical Society, Aug., 1978.

Fundamental Studies on the Corrosion of Ferrous Materials in Fused Salt System of Ammonium Bisulfate; T. Ishikawa: 5th Counterplan Research Committee on the Corrosion of Denox Plant in Iron Making Processes, Industrial Division, Society of Chemical Engineering of Japan, Sep., 1978.

Analysis on Performance of Discoidal Bipolar Electrode Cell in the Electrochemical Reduction of Potassium Dichromate Solution; T. Sasaki, S. Takeda and T. Ishikawa: The 1978 Fall Meeting of Electrochemical Society of Japan, Oct., 1978.

Effects of Cyclic Potential-sweep on the Electrochemical Passivation of Stainless Steels; T. Ishikawa: 7th International Congress on Metallic Corrosion (Rio de Janeiro), Oct., 1978.

Fundamental Studies on ALCOA New Smelting Process (Part 5) Influence of Solvent Salts on Current Efficiency; H. Ichikawa and T. Ishikawa: 12th Symposium on Molten Salt Chemistry, Nov., 1978.

Studies on the Properties of High Temperature Chloride Melts containing Aluminum Chloride (Part 2) Effect of Dissoluble Aluminum on the Electric Conductivity of Melts consisted of Equimole Mixture of NaCl- KCl as Solvent Melt; Z. Asano, S. Konda, T. Ishikawa and H. Ichikawa: *ibid.*, Nov., 1978.

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

T. Shindo, M. Otsuka, T. Kurachi, K. Nakagawa,
S. Kawakatsu, J. Masuko, K. Amemura, T. Itaya,
T. Oda, T. Sato and S. Nakao

Researches are carried out on various physico-chemical problems in this laboratory. Main subjects are listed as follows :

(1) Experimental studies continued on the hydrogen uptake of titanium, zirconium and their alloys. The effects of anodic pre-oxidation and solution impurities on the hydrogen absorption of these metals were observed under the condition of cathodic polarization. The most significant finding was the formation of needlike crystalline at the interface between the surface hydride and the metallic phase. This phenomenon was very remarkable for pure titanium, in which the grain size of metallic phase grew to about 1 mm by a proper thermal treatment. So-called Wagner's mechanism, which are usually assumed in kinetics of hydride layer growth must be corrected in considering this phenomenon.

(2) The anodic corrosion of Hastelloy family (high hickel alloys) was investigated in sulfuric acid solution. The ploarization characteristics and the dissolution rates of main component elements were measured. The effect of chromium and other element on the selective dissolution of molybdenum was discussed.

(3) The A. C. impedance of anodically polarized zirconium was measured in ammonium nitrate solution. The measurement system, which covered wide frequency range from 10^{-3} to 10^{4} Hz by an unified procedure, was developed. Computerized data processing was adopted for the elimination of noise in measurement

and the estimation of the impedance parameters. A micro-computer system, which transports the informations recorded in a wave-memory unit to a floppy-desk, was also developed.

(4) A Mössbauer-spectroscopic method for the identification of components in iron rust was proposed, and it was found that the differentiation could be clearly made between β-FeOOH and the superparamagnetic hematite by examining the change of mössbauer spectrum due to the calcination of iron rust sample at temperature near 300°C. These components behaved similarly in the test which was proposed by M. J. Graham and M. Cohen (Corrosion-NACE (1976)). An equipment for Mössbauer spectroscopic measurement at high temperature is being constructed, and it will be utilized in the kinetic studies of oxidation and other various reactions on iron and steel surfaces.

(5) Radioactivation analysis with the 45 MeV electron linear accelerator was adopted for the study on the adsorption of uranium by titanium oxide adsorbent. Sensitivity of analysis was much improved by modifying the design of converter which converts electron to neutron. Thermal neutron flux is expected to attain up to 10^{10} n/cm^2/sec soon by a further modification of converter.

(6) Kinetic studies of the oxidation of HTGR fuel particles continued this year. Adoption of the rate law equations for heterogeneous reaction of varying interface area was examined. Dissolution of HTGR fuel particles was also investigated in mixed solutions of nitric and hydrofluoric acids.

Oral Presentations

Effect of Surface Treatment on Hydrogen Uptake in Zirconium; T. Kurachi, T. Mizuno and T. Morozumi: The Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1978.

Activation Analysis of Gallium in Aluminium Ingot; H. Narita and T. Morozumi: The 1978 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Feb. 1978.

Rate Law in Oxidation of UO_2 Fuel Particle; M. Nabeshima, H. Ohashi and T. Morozumi: *ibid.*, Feb. 1978.

Thermal Transformation of Ferric Oxyhydroxide; H. Ohashi, M. Otsuka and T. Morozumi: *ibid.*, Feb. 1978.

Influence of Anodic Oxide Film on Hydrogen Absorption in Zirconium; T. Mizuno, T. Kurachi and T. Morozumi: Annual Conference of Japan Society of Corrosion Engineering, May 1978.

Role of Needlike Crystalline in Growth of Titanium Hydride Layer; K. Shindo and T. Morozumi: *ibid.*, May 1978.

A. C. Impedance of Anodically Oxidized Zirconium; M. Moriya and T. Morozumi: *ibid.*, May 1978.

Anodic Corrosion of High Nickel Alloys in Sulfuric Acid Solution; M. Moriya, K. Nakagawa, S. Tsurumi and T. Morozumi: *ibid.*, May 1978.

Activation Analysis of Gallium in Aluminium Ingot with 45 MeV Electron Linear Accelerator; H. Narita and T. Morozumi: The 15th Meeting on Isotope Research in Science and Technology, June 1978.

Measurement and Analysis of A. C. Impedance of Passive Film on Zirconium; T. Morozumi and M. Moriya: The Meeting of Project Pesearch on Metal Corrosion, Faculty of Engineeing, Hokkaido University, Dec. 1978.

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

Prof. Dr. K. Nishida, Assist. Prof. M.S. K. Atarashiya
Dr. T. Narita and Mr. K. Sugawara

Students

S. Karasawa, K. Sakurai, and K. Kurokawa
K. Kitajima, H. Takayama, Tsuda
A. Hiranuma and T. Nishizawa

The research carried out in this laboratory consists of two parts, that is, the first is the diffusion coating of metals to keep the metals safe against oxidation. The other is dealing with oxidation and sulfidation of alloys. The detail of these researches is as follows:

1) Diffusion coating of Ta sheets in Al vapor generated from $FeAl_2$ was performed in an evacuated quartz ampoule and the diffusion-treated sheets were examined by high-temperature oxidation in air for 50 hrs. Preliminary oxidation treatment to the sheet at 1100°C for 1 hr showed a good anticorrosion property at 900° and 1000°C, having no variation in weight and its microstructure, while for 1100°C corrosion oxidation does not proceed, but some voids originated in the alloy layer. Nb metal sheets were also calorized by the same method as described before. At 1100°C the best stability against oxidation was obtained. Further, V metal sheets were treated on its surface by many techniques to form diffusion coatings. But no best method has been found until now.

2) Oxidation of Co-Mn alloys (17 wt% Mn) in various oxygen partial pressures ($1 \sim 10^{-4}$ atm) was carried out. At a low oxygen pressure the oxidation kinetics still obeys a parabolic rate law, but the metal/scale interface shows an internal oxidation and a thick inner layer is formed.

Sulfidation of Fe–Mn alloys (11, 28, and 48 wt% Mn) were sulfided in the H_2-H_2S gas atmosphere ($Ps_2=10^{-4}\sim10^{-8}$ atm) at 700～1000°C. All kinetics obey a parabolic rate law, but, 48% Mn alloy shows the internal sulfidation and a thick inner layer at 1000°C.

3) Interdiffusion in Al_2O_3-Ta_2O_5 system was continued from the last year in connection with a good resistance of calorized Ta sheets against oxidation. But the preliminary treatment for sintering of each oxide is not perfect and also the volume change accompanied during diffusion in this system is rather great, so that the precise diffusion coefficient in Z type solid solutions could not be obtained, although a diffusion phenomenon by the formation of a terminal solid solution of Ta_2O_5 has been observed at 1500°C for 50 hrs. It is necessary to use big single crystals for such a diffusion experiment.

This year some events occurred in this laboratory : First, the research student by Japanese Government Scholarship, Assist. Prof. Dr. K. Godlewski of Academy of Mining and Metallurgy in Cracow, Poland, has visited in the end of March from Osaka Univ. of Foreign Affairs in order to study "High-temperature sulfurization of some Fe-Mn alloys" in this laboratory. He will stay about one year. Second, Dr. Narita, the instructor of this laboratory, has visited McMaster University in Canada in July, in order to work with Prof. W. W. Smeltzer. He is going to stay there about one year with his family. Next, Prof. K. Nishida attended the 153rd Electrochemistry Seattle Meeting in May 22-26 and presented the paper entitled "High-temperature Oxidation of Fe-Mn Alloys". He contacted many researchers with whom he was intimate. Last, Prof. R. A. Rapp of The Ohio State University visited with us in December and presented a special lecture entitled "Electrochemistry of Dry Corrosion". He stayed with us for a week in Sapporo.

Oral Presentations

Oxidation of Calorized Ta Sheets (II) : M. Hachinohe and K. Nishida : The 13th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1978.

Interdiffusion in α Phase of a Cu-Zn System by Zn Vapor (I): T. Narita and K. Nishida; The Spring Meeting of the Japan Institute of Metals, April, 1978.

Decomposition of Diffusion Coating Layer Formed on Metal During Oxidation (I); T. Narita and K. Nishida: *ibid.*, April, 1978.

Interdiffusion in α Phase of a Co-Sb System; T. Yamamoto, T. Takashima and K. Nishida: *ibid.*, April, 1978.

Oxidation Behavior of Co-base Alloys (Poster Session); K. Nishida and T. Narita: The Spring Meeting of Iron and Steel Inst. of Japan, April, 1978.

Occurrence of Cracks in Pressed Iron Oxide Mixed with Impurity Oxides During Their Hydrogen-Reduction Process; Y. Suzuki, S. sayama, Y. Nishikawa and K. Nishida; *ibid.*, April, 1978.

High-Temperature oxidation of Co-Mn Alloys; K. Nishida, T. Narita and S. Karasawa; The 153rd Seattle Meeting of Electrochemical Society in May, 1978.

High-Temperature Corrosion of Pure Iron in So_2 Gas; T. Shibata, T. Narita and K. Nishida; The Hokkaido Section Meeting of JIM and ISIJ, June, 1978.

High-Temperature Oxidation of Co-based Alloys (II); S. Karasawa, T. Narita and K. Nishida: The Fall Meeting of Japan Institute of Metals, Oct., 1978.

Anticorrosion Property of V Sheets by Surface Treatments: K. Sakurai, T. Narita and K. Nishida: *ibid.*, Oct., 1978.

Interdiffusion in ζ Phase of a Ni-Al System; T. Yamamoto, T. Takashima and K. Nishida; *ibid.*, Oct., 1978.

High-Temperature Corrosion of Iron and its Alloys in SO_2 Gas; K. Kurokawa, T. Narita and K. Nishida: The Hokkaido Section Meeting of JIM and ISIJ, Nov., 1978.

Oxidation of Ni at 1000~1300°C; K. Godlewski and K. Nishida: *ibid.*, Nov., 1978.

On the Utilization of Reduced Iron Powder Containing Gangues into Powder Metallurgy; Y. Suzuki, S. Sayama and K. Nishida: *ibid.*, Nov., 1978.

High-Temperature Sulfurization of Stainless Steels; K. Nishida and T. Narita: Special Research in Hokkaido University: Dec., 1978.

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

Prof. Dr. T. Tanaka, Assist. Prof. T. Nagai, Mr. H. Kiuchi,
Mr. R. Shibayama and Mr. S. Tasai

Students

K. Kaneko, K. Higashioka, I. Nakamura, H. Oshima,
K. Ominami, N. Tsuchida, T. Mori, K. Yoshida
and F. Doi

This laboratory is concerned with basic and applied researches on pyro- and hydrometallurgical extraction of nonferrous metals. Researches in progress are concentrated on the following projects:

(1) Utilization of sulfides for the production of hydrogen from water.

- i) Reaction of water vapour with metal sulfide. Reactions between steam and a metal sulfide such as Ag_2S, CaS, and ferrous sulfide are being carried out within the temperature range 900～1100°K by monitoring the evolved H_2 for the purpose of H_2 production from water.
- ii) Researches on thermochemical splitting of hydrogen sulfide. Thermochemical splitting of hydrogen sulfide by the following two combination reaction is being investigated:

$$MS_x + H_2S = MS_{x+1} + H_2$$
$$MS_{x+1} = MS_x + S^\circ$$

Cyclic treatments of hydrogen sulfide by combination of the following two reactions are also in progress:

$$M + H_2S = MS + H_2$$
$$MS = M + \frac{1}{2} S_2(g)$$

(2) Researches on the treatment of sulfide ores through hydrogen.

- i) Reduction kinetics of metal sulfides with hydrogen. This study is aimed at finding the mechanism of direct reduction of sulfide ores. Observation of morphologic characteristics of the metals formed from solid sulfides, or vapour phase sulfides are being made.

ii) Reduction of metal sulfates with hydrogen. The reverse reaction of hydrogen reduction of metal sulfates, related to the thermochemical decomposition cycle of water, has been recently noted in the energy field. Furthermore, since the hydrogen reduction of metal sulfates proceeds under a relatively low temperature as 300°C, the application of low-grade energy to metallurgy is expected. Measurements of reduction rate, identification of reduction products and reduction mechanism are being investigated on $CuSO_4$, $NiSO_4$, and $CoSO_4$.

(3) Purification of copper electrolyte

A novel process for this purpose has been investigated to remove arsenic in copper electrolyte by solvent extraction and to recover arsenic trioxide from strip solution by freeze-melt technique.

Oral Presentations

Thermochemical Decomposition of Hydrogen Sulfide by Cyclic Reactions; H. Kiuchi, T. Iwasaki, and T. Tanaka: The 7th Meeting of the Hokkaido Section of the Japan Electrochem. Soc., Jan. 1978.

Reduction Mechanism of Metal Sulfate with Hydrogen (III); R. Shibayama, K. Kaneko and T. Tanaka: The 1978 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Fab., 1978.

A Study for the Recovery of Hydrogen from Hydrogen Sulfide by Sulfurization of Metal Sulfides (II); H. Kiuchi, T. Iwasaki, and T. Tanaka: *ibid.*, Feb., 1978.

Recovery of Arsenic Tri-oxide by Freeze-Melt Process; K. Higashioka and T. Nagai: *ibid.*, Feb., 1978.

Reduction Mechanism of Metal Sulfate with Hydrogen (IV); R. Shibayama, K. Kaneko and T. Tanaka: Annual Meeting of the Min. Met. Inst. Japan, April 1978.

Reduction Mechanism of Metal Sulfate with Hydrogen (V); R. Shibayama, K. Kaneko and T. Tanaka: *ibid.*, April, 1978.

A Study for the Effective Utilization of Hydrogen Sulfide; H. Kiuchi, T. Iwasaki and T. Tanaka: *ibid.*, April, 1978.

Wet Process for Production of Arsenic Tri-oxide; K. Higashioka and T. Nagai: *ibid.*, April, 1978.

Purification of Copper Electrolyte via Solvent Extraction for Arsenic; M. Kobayashi and T. Nagai: *ibid.*, April, 1978.

Mutual Reaction between Lead Sulfide and Sulfate; H. Kiuchi, I. Nakamura and T. Tanaka: The 1978 Spring Meeting of the Hokkaido Section of the Min. Met. Inst. Japan, June, 1978.

Reduction Mechanism of Metal Sulfate with Hydrogen (VI); R. Shibayama, K. Kaneko and T. Tanaka: *ibid.*, June, 1978.

Removal and Recovery of Arsenic in Copper Smelter; K. Higashioka and T. Nagai: *ibid.*, June, 1978.

Process for Treatment of Arsenic Solutions; K. Higashioka and T. Nagai; Fall Meeting of the Min. Met. Inst. Japan, Oct. 1978.

Thermochemical Decomposition of Hydrogen Sulfide by Metals; H. Kiuchi, I. Nakamura and T. Tanaka: The 1978 Autumn Meeting of the Hokkaido Section of the Min. Met. Inst. Japan, Nov., 1978.

Anode Slime from Electrolytic Refining of lead; T. Tanaka: Invited Lecture at the 3rd Symposium on Non-Ferrous Extractive Metallurgy, Japan Society for the Promotion of Science, Nov., 1978.

Fixation of Sulfur by the Thermochemical Splitting of Hydrogen Sulfide; R. Shibayama and T. Tanaka: Research Committee for Fixation of Sulfur, Min. Met. Inst. Japan., Nov., 1978.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

Y. Sugawara, K. Miyagi, Y. Izumi, T. Ishida,
M. Katōno, M. Nakazaki, S. Horita
and A. Watanabe

In this laboratory, researches being conducted are mainly on the mechanical properties and growth characteristics of cast iron. Besides, some experiments on bending creep of steel and case-hardening of sintered iron were performed.

Research subjects are as follows :

(1) Bending strength of circular plates made of cast iron were tested under the distributed central load, and the experimental results were analyzed according to the non-elastic mechanical behavior of cast iron. Effects of plate dimension, grade of cast iron and diameter of central load on the rupture strength were formulated for the practical use in designing.

(2) Notch strength of cast iron was tested at room and liquid nitrogen temperature. Stress-strain property varied from nonlinear to almost linear by lowering the test temperature. Accordingly the rupture strength of notched bars decreased significantly and the fracture mode of casr iron was almost brittle at the lower temperature.

(3) In order to clarify the rupture properties of cast iron, FEM was applied on stress analysis in the circular plates and notched bars, Results showed that the stress distribution in the bending plate and notch-section varied with dimension of specimen, grade of cast iron and test temperature. And about the rupture strength

either the mechanical notch or internal notch of graphite flakes act preferentially according to these factors.

(4) Image analysis by a quantitative television microscope was applied on the distribution of graphite nodules in S. G. iron. By a mathematical procedure using a computer, a two-dimensional distribution of graphite nodules observed by microscope was converted to a volumetric distribution of them. Some experimental results of graphite nodule distribution suggested that the graphite nodule in S. G. iron may be formed in two different ways.

(5) Case-hardening of sintered iron by heating in dilute atmosphere was re-tested by a more practical process using a oxygen pump which had been developed recently. Experimental results showed that the sintered iron with graphite was case-hardened in the dilute oxygen gas produced from air by the oxygen pump. Most effective concentration of oxygen in the gas was as low as 1%.

(6) In order to clarify the effect of oxygen on the growth mechanism of cast iron, some dilatation tests were carried in oxygen-argon mixed gases. The growth of flake cast iron FC 30 was remarkable in the range of below 7% oxygen concentration, and the peak of growth was at 4% oxygen. These results may suggest that the promotion of growth by the dilute oxygen atmosphere are due to a self-carburizing mechaniam by a reaction of graphite and oxygen.

(7) Isothermal dilatation tests of flake cast iron were carried in CO atmosphere at temperatures between 350°C and 950°C for 2 hrs. Cast iron FC 30 grew in both range of subcritical and austenitic temperature. In the subcritical range the growth was largest at 650°C, and was less at 750°C. Though the matrix was almost changed to ferrite at 750°C, pearlite in the iron was not decomposed at 650°C. Therefore the peak of subcritical growth was not due to the graphitization.

(8) Bending creep of tempered martensitic steel was tested at 200°C for 2 hrs. with high-temperature strain gauge. Primary strain ceased within 30 min. of heating by the stress level up to 30 kg/mm^2. The lower the tempering temperature of steel, the more the creep

strain. Consequently the strain measured may be cause by the phenomenon analogous to the press-tempering of steel.

Oral Presentations

Bending Strength of Cast Iron Circular Plates under Distributed Load; T. Noguchi, K. Nagaoka and Y. Sugawara: The 93rd Grand Lecture Meeting of the Japan Foundrymen's Society, May 1978.

On the Isothermal Dilatometric Curve of Cast Iron in Dilute Oxygen Atmosphere; M. Sōma and K. Nagaoka: The 93rd Grand Lecture Meeting of the Japan Foundrymen's Society, May 1978.

Effects of Stress-Strain Properties on the Notch Strength of Cast Iron; T. Nogouchi; The 27th Grand Lecture Meeting of the Society of Material Science, Japan, May 1978.

Application of FEM for the Strength of Cast Iron; T. Noguchi, Y. Sugawara and K. Nagaoka: the Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society, June 1978.

Effect of Oxygen Concentration in Heating Atmosphere on Growth of Cast Iron; M. Sōme and K. Nagaoka: The Hokkaido Section Lecture Meeting of Japan Foundrymen's Society, June 1978.

Changes of Graphite Phase of S. G. Iron at the Primary Stage of Growth; The 94th Grand Lecture Meeting of the Japan Foundrymen's Society, Oct. 1978.

Strength and Standards of Metallic Materials; K. Nagaoka: The 5th Course of Lecture for Mechanical Engineer in Hokkaido Section by the Japan Society of Mechanical Engineers, Oct. 1978.

PHYSICAL METALLURGY LABORATORY

Prof. Dr. T. Takeyama, Assoc. Prof. Dr. T. Shibata
Dr. H. Takahashi and Mr. H. Hachinoe

Students

S. Ohnuki, H. Murakami, T. Matuhashi, T. Hasegawa,
H. Ohkami, T. Yanagisawa, S. Suzuki,
T. Suzuki, and H. Yamada

At present, this laboratory is actively engaged in studying various metallurgical factors to controll void formation due to irradiation for metals and alloys, since it is an urgent necessity to assure the reliability of materials for nuclear reactors. Hydrogen induced cracking in iron and iron-base alloys and stress corrosion cracking of titanium and stainless steels are also studied. Pit generation of high nickel alloys is analysed as a stochastic process. Details of the research subjects are as follows:

1) Void formation in Cu-1.5% Fe alloys induced by electron irradiation is found to be controlled by the formation of precipitates which are produced during irradiation or pre-irradiation aging. It can be rationalized that an interaction between precipitates and interstitial atoms concentrate vacancies around precipites so as to enhance void formation.

2) The effect of solute atoms on void formation has been studied on Cu–Ni alloys. The density of dislocations induced during electron irradiation increases with increasing of Cu content in the alloy. The increase in the dislocation density produced at pre-irradiation is also found to accelerate void formation. This fact indicates that change in the alloy composition contributes to stabilize dislocation arrays, through which void nucleation is controlled.

3) Radiation-induced precipitates in Ni–Nb alloys are analysed with TEM and energy dispersive X-ray microanalyser. The precipitates nucleated at stacking fault loops are identified as NbC,

which is supposed to form through enhanced diffusion of interstitial Nb atoms accompanying vacancies to combine carbon atoms.

4) Hydrogen charging into two phase Fe-Ni alloys induces blistering and microcracking. Electronmicroscopic observation clari-fies sites at which cracks nucleate.

5) Details of precipitation sites of hydrogen could be examined by TEM on iron-carbon alloys in which formation of incoherent and coherent precipitates of iron carbides is strictly controlled by a suitable aging treatment.

6) An etching technique for orientation pit formation for titanium is studied for the purpose of identifying fractured surface obtained in stress corrosion cracking. At a critical potential around active-passive transition in a HNO_3-HF solution, hexagonal facet pits are formed on basal plane of (0001).

7) Pit generation of Incoloy 800 alloy in 3.5% NaCl solution takes place by a combination of three parallel stochastic processes. Change in the pretreatment potential before pit generation is found to alter the transition probability of each process, resulting in the change of pitting potential. But a definite critical pitting potential could be obtained by the extrapolation of the potential sweep velocity to zero value for the pre-passivated surface attained at the more noble pretreatment potential than -0.10 volt.

In August, Professor Takeyama attended the 9th International Conference on Electronmicroscopy held at Montreal, Canada, and read a paper entitled Observation of Initial Cracking in Hydrogen Charged Pure Iron. Mr. Ohnuki, doctoral student, got a scholarship to attend the conference and read a paper on the Void Formation of Cu-1.5% Alloys during Irradiation in HVEM.

Oral Presentations

Pit Generation of Incology 800; T. Shibata and T. Takeyama: 13th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1978.

Behavior of Interstitial Solute Atoms during Void Formation; T. Takahashi and T. Takeyama: The Seminar on the Materials for Nuclear Reactor and Radiation Damage sponsored by Kyoto University, Nuclear Reactor Research Laboratory, Jan., 1978.

Hydrogen Charge in Iron-Nickel Alloys ; K. Matsuhashi, T. Takahashi and T. Takeyama : The Spring Meeting of the Japan Institute of Metals, April, 1978.

Void Formation of Cu-1.5% Alloy by Electron Irradiation ; S. Ohnuki, T. Takahashi and T. Takeyama : *ibid*, April, 1978.

Pit Generation Processes of Incoloy 800 ; T. Shibata and T. Takeyama : *ibid.*, April, 1978.

Pit Generation of High Nickel Alloys ; T. Shibata : The Meeting of the Cooperative Group on the Study of Stress Corrosion Cracking of High Nickel Alloys for Nuclear Power Plants, May, 1978.

Microcracks in Pure Iron due to Hydrogen Absorption ; T. Takahashi and T. Takeyama : The Seminar on Environmental Cracking of Metals, Jun., 1978.

Stress Corrosion Cracking of Titanium ; T. Shibata : *ibid*, Jun., 1978.

Pit Generation of Inconel 600 as a Strochastic Process ; T. Shibata and T. Takeyama : The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, Jun., 1978.

Void Formation of Ni-Cu Alloys by Electron Irradiation ; H. Ohkami, H. Takahashi and T. Takeyama : *ibid*, Jun., 1978.

Effect of Cu Addition on the Void Swelling of Nickel ; H. Ohkami, H. Takahashi and T. Takeyama : The 34th Meeting of Japan Society for Electronmicorscopy, Jun., 1978.

Void Formation of Cu-1.5% Fe by Electron Irradiation ; S. Ohnuki, H Takahashi and T. Takeyama : *ibid*, Jun., 1978.

Effect of Pretreatment on the Pitting Potential of SUS 304 and SUS 316 Stainless Steels ; T. Shibata and T. Takeyama : The 19th Corrosion and Prevention Symposium on Pretreatment of Stainless Steels, July, 1978.

The Voids Formation of Cu-1.5% Fe Alloys During Irradiation in HVEM ; S. Ohnuki, H. Takahashi and T. Takeyama :

Nith International Conference on Electron-Microscopy, Canada, Aug., 1978.

Observation of Initial Cracking in Hydrogen Charged Pure Iron; T. Takeyama and H. Takahashi, *ibid*, Aug., 1978.

Effect of Nitrogen on Stress Corrosion Cracking of Titanium; T. Shibata, T. Takeyama and K. Kurokawa: The Fall Meeting of the Japan Institute of Metals, Oct., 1978.

Effect of Solute Atoms on the Void Formation of Ni-Cu Alloys; H. Ohkami, T. Takahashi and T. Takeyama: *ibid*, Oct., 1978.

Void Formation of Cu-1.5% Fe Alloy by Electron Irradiation; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid*, Oct., 1978.

Statistical Evaluation of Stress Corrosion Cracking Data; T. Shibata: The 25th Symposium of Corrosion and Prevention, Nov., 1978.

Annealing Behavior of Voids formed in V-C Alloys due to Neutron Irradiation; S. Ohnuki, T. Takahashi and T. Takeyama: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, Nov., 1978.

The Voids Formation of Cu-1.5% Fe Alloy during Irradiation in HVEM

S. Ohunki, H. Takahashi and T. Takeyama

Proc. Ninth International Congress on Electron
Microscopy Vol. 1, 380 (1978)

Cu–Fr alloy aged at 973 K for several times were irradiated in the 650 kV EM at 523 K. On aged condition, a number of coherent and semi-coherent precipitates were observed and each specimen showed the different behavior of void formation. (a) In aged specimens, void number densities were propotional to the densities of precipitate but void swelling were lower than pure Cu. In a specimen aged for 4 days, most voids were formed near the preexisting precipitates. These phenomena suggest that the strain field formed in the interface between the precipitate and matrix would act as the preferential sink site for irradiation induced defects and excess vacancies would aggregate near the interface and form the voids. (b) In the as-quenched specimen, three phenomena were observed. First, the void with low density were formed at about 3 dpa and fine precipitates were observed in the matrix and finally, other voids with high density were formed above 6 dpa. And then void swelling was lowest in this experiment. These phenomena of this specimen would be explained by the effect that in low fluence, the concentration of free vacancy reduced due to trapping by solute atoms. (English).

Observation of Initial Cracking in Hydrogen-Charged Pure Iron

T. Takeyama and H. Takahashi

Proc. Ninth International Cogress on Electron
Microscopy, Vol. 1, 602 (1978)

The purpose of the present work is to investigate the nucleation site and the structure of microvoid and microcrack which are formed in single and polycrystals by the precipitation of hydrogen gas during cathodically charging.

In order to observe the initiation of the microvoid and crack, both surface and inside structures of specimen were observed by aid of HVEM of 650 kV and SEM.

In polycrystal, microcracks mainly nucleated along grain boundary and propagated toward inside of a grain. At the tip wedge-shaped microcrack, strain contrast was often observed, and on surface of the cracks surface dislocation or ledge structures were observed. Also, in the specimen where dislocations were introduced by plastic strain, microvoids nucleated in the region of tangled dislocations.

On the other hand, in single crystals microvoids and cracks which propagated along (110) slip planes were observed.

The results of present work indicated that hydrogen atoms would be preferentially absorbed on slip and/or grain boundary and then the microcrack would initiate from the microvoid by the aid of hydrogen gas pressure in the process of accumulation of hydrogen atoms. (English)

On the Bending Strength of Cast Iron Circular Plates

T. Noguchi and K. Nagaoka

IMONO, **50**, No. 4, 217 (1978)

Bending strength of cast iron circular plates were examined using specimens of various strength, diameter and thickness. Cast iron disks did not fracture at the maximum load, but still supported the load with increasing deflexion. Conventional bending strength σ_{bp} defined by an elastic formula and the maximum load had good correlation with the tensile strength σ_t. It depended on the thickness of the disk h, but just slightly on diameter D. Thus the following equation was valid experimentally.

$$\sigma_{bp}=2\sigma_t+7+100/h \quad (\mathrm{kg/mm^2})$$

The strength of the disk is estimated by

$$P_m=\sigma_{bp}\cdot h^2/\left[3/2\pi+(1+\nu)\,(0.485\ln(D/2h)+0.52)\right]$$

The calculated values well agreed with the experimental values for lathed specimens of $\sigma_t=15\sim 35\ \mathrm{kg/mm^2}$, $h=5\sim 20\ \mathrm{mm}$, $D=200\sim 400\ \mathrm{mm}$. The formula was also valid for as cast disks in the region of $\sigma_t<25\ \mathrm{kg/mm^2}$ where σ_t is not the strength of the standard test piece, but is that of the casting. (Japanese)

On the Thermal Conductivity of Cast Iron with Various Graphite Configurations

T. Noguchi, Y. Matsumoto and K. Nagaoka

Bulletin of the Faculty of Engineering, Hokkaido University, **No. 87,** 57 (1978)

In order to investigate the role of graphite flakes on the thermal conductivity of cast iron, ferritic irons with various chemical compositions and graphite configurations were examined by the step-heating method. The effect of graphite flakes was expressed by the ratio λ_e/λ_c, where λ_e was the measured conductivity of the iron and λ_c was the conductivity of the matrix estimated from its chemical compositions.

The value of λ_e/λ_c was $1.7\sim2.4$ in flake graphite iron. The values increased with increase in carbon content, the increase in coarseness and the length of graphite flakes. In spheroidal graphite iron, λ_e/λ_c was $1.03\sim1.15$, and only slight increase was seen with the increase in carbon content. The role of eutectic D-type graphite was almost the same as in the case of flake graphite. The iron with less spheroidized wormtype graphite showed higher λ_e/λ_c values than fully spheroidal iron.

Form factor ψ was introduced according to Hamilton's method for the evaluation of the effect of graphite shape. A correlation was observed between λ_e/λ_c and the value of ψ calculated in some specimens. It is suggested that, in addition to the graphite shape, the remarkable difference in conductivity may be caused by the anisotropic structure of the graphites, and graphite-matrix coherency. (Japanese)

Observation of Cracks around Graphite Flakes of Cast Iron Heated in CO Atmosphere

K. Nagaoka, T. Noguchi, M. Sōma and K. Suzuki

Journal of The Japan Insititute of Metals,
42, No. 8, 821 (1978)

Microstructure of flake graphite cast iron heated to 950°C in CO atmosphere was observed by optical and electron microscope. The cast iron grown in CO showed hairline structure in the matrix around graphite flakes. And at the hairline no carbon was detected and some concentration of oxygen and silicon was revealed by X-ray scanning analysis.

It was clarified by the observation with scanning electron microscope that the hairline was a crack of metallic matrix and at the crack-tip there formed an alignment of dots with space interval of less than 1 μm. Although the line up of point defects looks like the boundary cavitation which is a type of high-temperature fracture, such minute cavitation is unusual. So a possible mechanism proposed for the present discontinuous fracture is that due to the plurality of double dislocation pile up in mode II sliding. (Japanese)

On the Strength and the Stress-Strain Propertied of Gray Cast Iron at Low Temperatures

T. Noguchi and K. Nagaoka

IMONO, **50,** No. 9, 560 (1978)

Low temperature strength and stress-strain properties of gray cast irons were examined under tension and compression. The strain gauge method was employed on pearlitic and ferritic irons in the temperature range of +20°C to −196°C. Just as reported so far, the present experiments showed that the tensile strength, the proof strength and the elastic modulous increased by lowering the test temperature. Down to the temperature of −150°C, the tensile fracture strain decreased indistinctly in most irons except for the ferritic one which showed the maximum value at −100°C. At −196°C, the fracture strain was reduced to as small as 0.4% in all irons. The stress-strain curves shifted to a higher stress level by decreasing the temperature, i. e., gradually down to −150°C and rapidly at −196°C. The shift of the curves were almost at the same rates both in tension and in compression. Such charracteristics of gray cast irons at low temperatures were well expressed by factors a and b of the hyperbolic formula $\sigma = b\varepsilon/(a+\varepsilon)$ which approximates the stress-strain relation. Furthermore, SEM fractography revealed that the transition in the fracture appearance occured at about −150°C in ferritic irons, and in a ferritic iron there were some dimple patterns even at −196°C. (Japanese)

On the Isothermal Dilatation Curves of Cast Iron in Dilute Air-Argon Gases

K. Nagaoka and M. Sōma

Report of Project Research on Metal Corrosion,
Faculty of Engineering, Hokkaido
University, P 26, Sept. (1978)

In order to elucidate the effect of dilute oxygen in heating atmospheres on the dimensional irreversibility of cast iron at high temperature, tests on isothermal dilatation curves at 950°C were carried on as-cast and pre-grown flake irons in vacuum, argon and air-argon mixed gases of various oxygen concentration. Results obtained are as follows;

(1) In vacuum all irons contracted during isothermal heating. Marked contraction was observed in low strength and pre-grown irons.

(2) In air-argon mixed gases the isothermal contraction of iron decreased, and in 2.0% oxygen mixed gas the pre-grown iron dilated isothermally.

(3) Microstructures of irons heated in dilute oxygen atmosphere showed the zone of pearlitic matrix under the decarburized surface zone of ferrite. The appearing of pearlitic zone was promoted in low strength and pre-grown iron, and by the increase of oxygen concentration in heating atmosphere.

(4) The 5% pre-grown iron showed the maximum isothermal dilatation in the 2.0% oxygen mixed gas, and in more than 5.0% oxygen gas the dilation increased gradually. Such discontinuous effect of dilute oxygen in atmosphere is analogous to its effect on the growth of cast iron by cyclic heating. (Japanese)

X-ray Analysis of Flake Graphite Iron Grown in CO Atmosphere

K. Nagaoka, M. Sōma and K. Suzuki

The HITACHI Scientific Instrument News,
21, No. 4, 2, (1978)

In order to reveal the mechanism of serious growth of flake cast iron in CO atmosphere, some behaviors of carbon by heating was pursued according to observation of structure and scanning analysis by SEM-XMA. During the heating in CO, flake cast iron was carburized; and the longer the the heating-time and the higher the temperature, the more the carbon pick-up and the growth.

Structural changes in grown irons are the corpulence of graphite fiakes and appearing of hairline in the matrix. These changes were more evident in the iron more grown. SEM-XMA had revealed clearly that the corpulence of graphite flakes was due to the precipitation of carbon around the graphite flake. But at the hairline no carbon was detected and some concentration of oxygen and silicon was analyzed.

SEM observation of the hairline around graphite flake showed that the line was a crack occurred in the matrix. And Besides the ordinary high-temperature crack an alignment of small points was observed at the tip of the hairline crack. Though the dotted line defects looks like the boundary cavitation by creep rupture, so fine line up of boundary cavities were not observed yet. (Japanese)

SEM Fractography of Gray Iron Fractured at Low Temperatures

T. Noguchi and Y. Sugawara

Bulletin of the Faculty of Engineering, Hokkaido
University, **89,** 51 (1978)

SEM observation was carried out on pearlitic and ferritic gray irons fractured in low temperature range of +20°C to −196°C, and the correlation of fracture morphology with the strength and stress-strain properties were considered. The feature of a fracture surface was expressed by the fractional area of ductile facets to the whole fractured matrix.

The ductile fracture ratio was almost 1.0 near room temperature, and with the lowering of the test temperature, the ratio decreased by increasing the cleavage area.

The transition temperature of ductile to cleavage in ferritic iron was about 50°C lower than in pearlitic iron. Although the ratio was almost zero at −196°C, ductile fracture was observed to a certain extent in ferritic iron.

The change of fracture appearance, however, was not necessarily correlated to the stress-strain properties. For example, while the fracture was mostly cleavage at −150°C, the fracture strain was the same as that at room temperature. And the fracture, in which cleavage and trans-granular facets were predominant, was followed by the ductile stress-strain properties. (Japanese)

Probabilistic Evaluation of Localized Crrosion

Toshio Shibata

Corrosion Engineering (Boshoku Gijutsu)
27, No. 1, 23 (1978)

Probabilistic nature is intrinsic for localized corrosion and important for evaluating the corrosion loss in laboratories or practical fields, so that several types of probability distribution function (pdf) were reviewed with examples of corrosion data. Normal, log-normal, Poisson, and exponential type of pdf were described for evaluating pitting potential, crevice potential, pit density, pit generation time, or failure time of stress corrosion cracking. Wide applicability of the extreme value distribution was emphasized. Recent works using Weibull pdf was suggested to bridge the gap between ;aboratory and field data of localized corrosion. (Japanese).

Multichannel Pitting Corrosion Testing Apparatus and its Applications

Toshio Shibata and Taro Takeyama

Corrosion Engineering (Boshku Gijutsu)
27, No. 2, 71 (1978)

A multichannel pitting corrosion testing apparatus has been developed to obtain a large number of data of pittng potential and induction time for pit generation, which are necessary for studying a statistical nature of pitting corrosion. The 12 channel type was developed, which operates with 1 potentiostat and 1 electrolytic cell containing 1 reference electrode, 1 counter electrode and 12 specimen electrodes. Each channel connecting to the specimen electrode is consisted of a current measuring unit, a relay switch and a timer. Pit generation on any specimen could be detected by an anodic current increase measured by the current measuring unit, which, in turn, gives a signal to the relay switch, when the current exceeds a pre-selected value, resulting in opening the circuit connecting to the pitformed specimen. The time passed from start to open is registered by the timer. Thus, 12 independent pit generation events could be determined in 1 experiment. Distribution of the pitting potential using the potential sweep method and the induction time for pit generation at a constant potential of commercial stainless steels and high nickel alloys in 3.5% NaCl were illustrated. (Japanese).

Pit Generation of Inconel 600 as a Stochastic Process.

Toshio Shibata and Taro Takeyama

Journal of the Japan Institute of Metals,
42, 743 (1978)

Pit generation of Inconel 600 in 3.5% NaCl solution at 35°C has been analyzed by a stochastic theory which has been developed for explaining a statistical variation in strength or delayed time for the fracture of solid materials. A large number of measured values of pitting potential by a potential sweep method and induction time for pit generation at a constant potential were obtained with the aid of a multichannel pitting corrosion testing apparatus. The pit generation process of Inconel 600 is found to consist of a parallel combination of two independent processes, each pit generation rate(λ_1 and λ_2) being simply defined by the potential (E) as follows: $\lambda_1=20.4\ (E-0.378)$, $\lambda_2=1.11\times10^{-13}\exp(64.2\,E)$. The first process having a linear dependence of the pit generation rate on the potential is concluded to control pit generation during the potential sweep. For this case the most probable value of pitting potential ($\bar{E}$) increases with square root of the potential sweep velocity (v), i. e., $\bar{E}=0.221\ v^{1/2}+0.378$. The linear potential dependence of λ_1 suggests that not an electrochemical but a mechanical break-down of passive film due to the electrorestriction force is responsible for pit generation. (Japanese)

Electrochemistry of Wet Corrosion

T. Ishikawa

Corrosion Engineeing (Boshoku Gijutsu),
27, No. 3, 139 (1978)

In this article, as a part of guide series for introduction to metallic corrosion, various cases of natural corrosion were explained by superposing of the polarization curves for anodic reaction of corroding metals and for cathodic reaction of reducible agents dissolved in corrosive medium.

Similar electrochemical explanation were also carried out on the heterogeneous corrosion such as gavanic and differential aeration corrosion. (Japanese)

Anodic Oxidation of Cobalt in Neutral and Basic Solutions

Norio Sato and Toshiaki Ohtsuka

J. Electrochem. Soc., **125,** No. 11, 1735 (1978)

The anodic oxidation and anodic oxide films of cabalt have been studied in borate buffer solutions in the pH range from 7 to 11. The anodic polarization curve shows the active dissolution, primary passivity, secondary passivity, tertiary passivity, and transpassivation. It is also shown that the anodic oxide film is hydrated oxide of CoO in the primary passive region, bilayered oxide CoO/Co_3O_4 in the secondary passive region, and bilayered oxide of CoO/Co_2O_3 in the tertiary passive and transpassive regions. The dissolution current of the anodic oxide film in the secondary and tertiary passive is much smaller than that in the primary passive region. By cathodic reduction the outer Co_2O_3 layer is first converted to Co_3O_4 and then reduced further to hydrated Co^{2+} ions before the inner CoO layer is reduced to metallic cobalt. (English)

The Composition and Layer-Structure of Passive Films on Iron in Neutral Solution

Rokuro Nishimura and Norio Sato

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 91,** 125 (1978)

The passive films formed on iron in neutral borate and phosphate solutions of pH 8.42 were investigated by using electrochemical and ellipsometric techniques. From analyses of iron dissolution and δP-δA curve during galvanostatic cathodic reduction of the film, it was found that the passive films formed in these solutions consisted of a deposit layer next to the solution and a barrier layer in contact with the metal. In borate solution, the deposit layer was hydrated iron (III) oxide at relatively noble potentials and hydrated iron (II–III) oxide at less noble potentials. Furthermore, the barrier layer composition changed from iron (II–III) oxide at potentials below the Flade potential to iron (III) oxide at more noble potentials. The thickness of the barrier layer increased nearly linearly with the potential. In phosphate solution, the deposit layer was of the same nature as that in borate solution, but the barrier layer always contained iron (II) ions with mean oxidation valency $Z_{Fe}=2.33$.

It was also found for the passive film in borate solution that there was an iron enrichment or depletion at the deposit/barrier interface and that an adsorption layer of OH radical was probably formed at the doposit/solution interface. However, no such adsorption layer and iron depletion (or enirchment) were found in the passive film formed in phosphate solution.

The results were explained by assuming an anion selective property for the film formed in borate solution and a cation selective property for the film formed in phosphate solution. (Japanese)

Time Variation of the Thickness and Composition of Passive Films on Iron in Neutral Borate Solution

Rokuro Nishimura and Norio Sato

Corrosion Engineering (Boshoku Gijutsu),
27, 457 (1978)

The composition and the thickness of passive films on iron in a neutral borate solution at pH 8.42 have been investigated as a function of anodic oxidation time extending from 30 seconds to 25 hours at two different potentials, 0.025 V and 0.845 V (S. H. E.), by using ellipsometric and electrochemical techniques.

The loci of δP–δA relationship obtained from ellipsometric measurements consist of two lines with different slopes, which shows that passive film is a two-layered film composing of a deposit layer and a barrier layer. The loci of $W_{Fe^{2+}}$–Q_C relationship given by the film dissolution measurements by means of cathodic reduction in a solution of pH 6.48 at constant current also show a two-layered film in agreement with the results of ellipsometric measurements.

The compositions and thicknesses of the deposit layer and the barrier layer formed at 0.025 V vary with anodic oxidation time. For passive films formed at 0.845 V, the deposit layer exhibits almost no change in its composition and thickness with anodic oxidation time, while the barrier layer thickness increases with time and its composition changes from magnetite-like oxide to ferric oxide in an initial period of 1 hour.

There occurs depletion or enrichment of iron ions (oxygen ion excess or deficient) at the deposit/barrier layer interface and the degree of depletion or enrichment is found to depend on the anodic oxidation time.

Discussions are made on the formation and growth of the deposit layer and the barrier layer and also on the generation of a depletion layer and a enrichment layer at the deposit/barrier interface. (Japanese)

In-Depth Profiles of Anodic Oxide Films on Fe–Ni Alloy in Boric Acid-Sodium Borate Solutions

Masahiro Seo and Norio Sato

Corrosion Science, **18,** No. 7, 577 (1978)

The in-depth profiling of anodic oxide films formed for 1 h on a 55 Fe–45 Ni alloy in boric acid-sodium borate solutions was made by the simultaneous use of AES (Auger Electron Spectroscopy) and sputter-etching with Ar^+ ion to determine the thickness and composition of anodic oxide films and to elucidate the experimental variables which affect them. The anodic oxide film was thicker and richer in the Fe component in pH 6.48 solution than in pH 8.45 solution. It was estimated from the in-depth profile of the anodic oxide film that a significant part of the Fe component in the anodic oxide film was in the di-valent state. Enrichment of the Ni component at the oxide/substrate interface and depletion of Ni component in the film were measured as function of pH and anodic potential. These results are explained in terms of the combination of the following factors : (i) preferential dissolution of the Fe component, (ii) preferential oxidation of the Fe component, and (iii) preferential anodic deposition of the Fe or Ni component. (English)

Differential Composition Profiles in Depth of Passive Films on Iron-base Alloys

Masahiro Seo and Norio Sato

Corrosion Engineering (Boshoku Gijutsu),
27, 647 (1978)

A differential method for measuring number of component atoms in surface atomic layers by use of AES and argon sputter-etching was applied to the analyses of thin anodic oxide films formed on Fe–30 Cr alloy, 304- and 316-stainless steels in deaerated 0.5 M sulfiuric acid solution. From the measured composition profiles in depth, the surface excess, Γ_{Cr}, Γ_{Ni}, Γ_{O} and Γ_{S} on the dividing surface with $\Gamma_{Fe} \approx O$ was estimated as a function of anodic potential.

In the passive potential region, the surface excess changes depending on the species of alloys as follows: $\Gamma_{Cr}=1\sim3\times10^{15}$ atoms/cm^2, $\Gamma_{Ni}=4\sim8\times10^{14}$ atoms/cm^2, $\Gamma_{O}=3\sim6\times10^{15}$ atoms/cm^2 and $\Gamma_{S}=2\sim8\times10^{14}$ atoms/cm^2. The surface excesses of chromium and oxygen, Γ_{Cr} and Γ_{O} of 316 stainless steel are smaller than that of 304 stainless steel, indicating that molybdenum affects Γ_{Cr} and Γ_{O}. The effect of molybdenum on Γ_{Cr} and Γ_{O} was discussed in connection with the electrochemical characteristics of molybdenum during passivation. (Japanese)

Electrochemical Behaviour and Structure of Anodic Oxide Films Formed on Aluminium in a Neutral Borate Solution

H. Takahashi and M. Nagayama

Electrochim. Acta, **23,** 279 (1978)

99.99% Al specimens were anodically oxidized in a boric acid-borate solution (pH=7.4) at temperatures of 20, 40 and 60°C, by applying a constant potential of 50 V (vs sce). The anodic current and the amount of dissolved Al ions were measured as a function of the anodizing time. Observations of sections of the oxide films were made by electron microscopy using an ultra-microtome for sample preparation. The current was found to decrease exponentially with time to a steady value which increases with increasing temperature. The current effeciency for the formation of oxide decreases gradually with decreasing current and is less than 70% in the period with steady current. The low efficiency of the reaction is exclusively due to the field-assisted dissolution of the oxide. In general, the oxide film is composed of two layers. The inner layer next to the metal is compact and is responsible for the polarization behaviour, its thickness being almost constant during anodizing but increasing with decreasing solution temperature. The outer layer, on the other hand, has many vertical pores and continues to grow even in the period with steady current. The porosity of the outer layer is estimated to be 22% for 40 and 60°C films and the 60°C film contains 4.5% bound water. The current-potential relationships measured for the anodized specimens in a 20% solution indicate that the protective ability of the inner layer increases with increasing anodizing time and temperature. (English)

The Determination of the Porosity of Anodic Oxide Films on Aluminium by the Pore-Filling Method

H. Takahashi and M. Nagayama

Corr. Sci., **18,** 911 (1978)

The validity of the pore-filling method proposed by Dekker and Middelhoek to measure the porosity of anodic oxide films on Al was checked. Pore-filling was performed in an aqueous solution of boric acid-borate (pH=7.4, 20°C) by applying a constant anodic current of 0.5 mA/cm^2. It was found that the borate-glycol solution adopted by Middlehoek is not suitable because of anodic decomposition of glycol. The transport numbers for Al^{3+} and O^{2-} ions moving across the barrier layer were estimated to be 0.40 and 0.60, respectively. Using these values, the porosity of films anodically formed in a $H_2C_2O_4$ solution was determined. The time-variation in the porosity during chemical etching of a porous oxide was followed by this method. The results obtained were always consistent with those estimated by electron microscopy. In addition to the porosity, the thickness of the porous oxide up to 5000 Å could be determined by the pore-filling method. (English)

Measurement and Analysis of A. C. Impedance of Passive Film on Zirconium

Takashi Morozumi and Makoto Moriya

Report of Project Research on Metal Corrosion,
Faculty of Engineering, Hokkaido
University, P49, Sept. (1978)

A. C. impedance of the potentiostatically anodized zirconium was measured in ammonium nitrate solution. The frequency range covered widely from 10^{-2} to 10^{4} Hz by adopting an unified procedure. Sinusoidal A. C. voltage with fixed amplitude less than 5 mV was applied in the potential setting branch of the potentiostat circuit, and both of the A. C. wave signals of the voltage and the current, which flowed between the specimen and the auxiliary electrode, were picked up with 2 2ch. wave memory unit. Displayed data with a tape puncher was processed by computerized curve-fitting and calculation. The curve-fitting was made by the non-linear least square method to eliminate the wave deformations such as noise and drift, and to reproduce undeformed sinusoidal voltage and current waves.

At the potnetial less noble than 1 V, in which the electrode process of the growth of anodic oxide film only existed, the impedance was almost linearly proportional to inverse frquency. In this potential region, the phase angle was almost 90° and the impedance had capacitive nature. The capacitance showed a slight change with frequency in general and its small dispersion was observed around a frequency between several and several tenth Hz. This dispersion, which indicated a distributed relaxation time spectrum, was explained with the ionic relaxation mechanism. In the potential region, in which the oxygen evolution occurred as well as the oxide formation, a purely resistive impedance was observed at low frequency. (Japanese)

Anodic Corrosion of High Nickel Alloys in Sulfuric Acid Solution

Makoto Moriya, Kazuto Nakagawa, Saburo Tsurumi
and Takashi Morozumi

Corrosion Engineering (Boshoku Gijutsu),
27, 653 (1978)

Various experimental techniques, such as the potentiostatic and the potentiokinetic polarization charachteristics measurements, the colorimetic analyses of dissolved alloy constituents and the electron microscopic observation, were adopted to study the anodic corrosion of high nickel alloys in 1 N sulfuric acid. Hastelloy B, which was the lowest in chromium content among five sorts of alloys used, showed no indication of passivation but poor corrosion resistance in the potential range investigated. Other four alloys passivated at the potential around 200 mV vs. S. C. E., and the higher chromium content resulted in less passivation current in general tendency. These observations led the conclusion that chromium played essential role in the passivation of the alloys. In the potential range around 600 mV vs. S. C. E., selective dissolution of moybdenum was observed with two sorts of alloys, namely Hastelloy C was the most remarkable in this behaviour and Hastelloy X less but slight. Localized attack was found surrounding the deposit of chromium carbide. The control of chromium depletion due to the decrease of carbon content or the increase of chromium content in alloy seemed to be effective in prevention of such selective attack of molybdenum. (Japanese)

Anodic Corrosion of Hastelloy-C in Sulfuric Acid Solution

Makoto Moriya, Kazuhito Nakagawa
and Takashi Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 86,** 57 (1978)

The corrosion behavior of anodically polarized Hastelloy-C was investigated in an 1 N sulfuric acid solution by using various methods as follows ; e. g. potentiostatic and potentiolinetic polarization characteristic measurements, colorimetric analyses of the dissolved alloy elements an ESCA method.

Both of the two kinds of polarization characteristic measurements gave results indicating that the alloy behaved in three different ways according to the potential from -0.2 to 1.0 Volt vs S. C. E. Below 0.2 V, although iron tended to selectively dissolve, the total amount of dissolution was very slight and the alloy was almost maintained in a passive state. At the potential between 0.2 and 0.8 V, local attack of the alloy and selective dissolution of molybdenum were observed. The electrolytic current reached its maximum value at 0.6 V and a steep rise of the current was observed at about 0.9 V. Above the latter potential, the alloy was uniformly attacked and all elements dissolved in proportional manner to their alloy contents. Different ESCA spectra were also obtained according to the polarization potential. (Japanese)

Corrosion Inhibitors for Copper and Copper Alloys

T. Notoya

Corrosion Engineering (Boshoku Gijutsu),
27, No. 12, 166 (1978)

This article is a review of recent literature on corrosion inhibitors for copper and copper alloys. Inhibitors are divided into two categories; (i) inorganic inhibitors, such as chromates, phosphates and ferrous ions and (ii) organic inhibitors which include heterocyclic organic compounds, i. e., benzotriazole (BTA) and mercaptobenzothiazole (MBT) and their relative compounds. At present these are the most effective and widely used inhibitors in a variety of systems. The BTA derivatives such as tolytriazole (TTA) and benzotriazole carboxylic acid will be the mot promising inhibitors for copper and copper alloys. It is suggested that dimercaptothiadiazole (DMDTA) and triazinedithiol (TDT) and its derivatives may be used as a substitute of BTA. Effectiveness of both DMTDA and TDT is found to be better than BTA in some corrosive environments. Significant role of oxide films present on the metal surfaces is stressed in order to clarify the mechanism of protection performance of inhibitors. Long chain thio-compounds as film forming inhibitors are also described. (Japanese)

Surface Topography and the Corrosion Prevention of Copper by Benzotriazole

T. Notoya

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 89**, p. 11 (1978)

An electron scanning microscopic study was made on the surface topographies subsequent to immersion in 3% NaCl solution in specimens of both fine polycrystalline copper and coarse grained copper with a thin copper-benzotriazolate (CuBTA) film on the surfaces. The results indicate that corrosion initiates at active sites in the protective multilayer films of copper oxide and CuBTA. Protectiveness of the CuBTA films appeared to be related to the crystallographic orientation of the metal substrate and underlying oxide. (English)

Corrosion Pretreatment for Copper-Zinc Alloys

G. W. Poling and T. Notoya

The International Corrosion Forum Devoted Exclusively to the Protection and Performance of
Materials. Paper No. 44, March 6~10,
1978. Houston, Texas

Combination of four different types of zinc-complexing agents with benzotriazole (BTA), an efficient complexant and corrosion inhibitor for copper, were tested as pretreatment inhibitors for 70/30 and 60/40 brasses in aerated 3% NaCl solutions. Alkyl dithiocarbonates, of C_6 to C_8 chain length, proved superior to: 2, 5-dimercaptothiadiazole (DMTDA); sodium diethyldithiocarbamate (DDC) and sodium diethyldithiophosphate (DEDTP), in combination with BTA under a variety of test conditions. Apart from acting as an acid inhibitor for 70/30 brass exposed to acidic NaCl solutions, the DMTDA was also an effective partner inhibitor for BTA. Combinations of the other two complexing agents (DDC and DEDTP) plus BTA actually accelerated the corrosion of 70/30 brass but provided good protection of 60/40 brass in the NaCl solutions. Scanning electron micrographs showing surface topographies of test specimens with and without these inhibitor pretreatments are presented. Galvanostatic polarization curves are shown to help evaluate the inhibiting action of each inhibitor combination. (English)

Adsorption of Zn^{2+} Ions on Fe(III)-hydroxide

H. Tamura, M. Oshima, K. Go and M. Nagayama

Bulletin of the Faculty of Engineering. Hokkaido
University, **No. 91,** 139 (1978)

The extent of Zn^{2+} ion adsorption on Fe(III)-hydroxide prepared by hydrolyzing $Fe(NO_3)_3$ was measured as a function of the solution pH (5～7) and the amount of the hydroxide. Acid base titrations of the hydroxide were also carried out, and its surface area was measured by the BET method. It was found that the concentration of the adsorbed Zn^{2+} ions is proportional to the concentrations of Zn^{2+} ions in solution and Fe(III)-hydroxide, but is inversely proportional to the second power of the hydrogen ion concentration:

$$[Zn^{2+}_{ad}] = K\,[Zn^{2+}]\ [Fe(III)]/[H^+]^2$$

This behavior is explained by considering the adsorption reaction to be

$$Zn^{2+} + 2-FeOH \rightleftharpoons -(FeO)_2Zn_{ad} + 2H^+,$$

where $-FeOH$ is the site at which the Zn^{2+} ion can adsorb. The $-FeOH$ type site was found to prevail over the $-FeOH_2^+$ and $-FeO^-$ type sites in the pH region investigated, and the concentration of $-FeOH$ sites was much higher than that of the adsorbed Zn^{2+} ions. (Japanese)

The Effect of Precipitation Conditions on the Dissolution Characteristics of Fe (III)-Hydroxide in a Tartaric Acid Solution

H. Tamura, M. Oshima and M. Nagayama

Bulletin of the Faculty of Engineering Hokkaido
University, **No. 88,** 119 (1978)

Fe (III)-hydroxide was formed by precipitation from an $Fe(NO_3)_3$ solution and its dissolution behavior was examined in a 0.16 M tartaric acid solution (pH=1.90) at 25°C. The dissolution reaction invariably obeys the equation,

$$1-(1-x)^{1/3}=kt$$

where x is the fraction of the dissolved Fe (III) to the total Fe (III), t is the dissolution time and k is a constant.

The value of k is affected by the conditions under which Fe (III) hydroxide is prepared, ie., (1) kinds of alkalis used for precipitation, (2) pH after precipitation, (3) solution temperature and (4) aging time. It was found that k values are smaller for weaker alkalis, higher pHs and temperatures, and longer aging times. This is explained by considering Fe (III) hydroxide to form through (A) and (B), (A) nucleation and particle growth and (B) aggregation and dehydration of particles. When Fe^{3+} ions are brought in contact with weaker alkalis at higher temperatures, a smaller number of nuclei will be generated in (A) resulting in larger particles. These are more resistant to dissolution because of the smaller total surface area. In (B), the particles aggregate and dehydrate, and k decreases with time. The aggregation is facilitated with increasing pH bacause the positive surface charge of the particles decreases. Dehydration changes the nature of Fe (III) hydroxide to increase its resistivity to dissolution. (Japanese)

Kinetic Study on Dissolution of Uranium Oxides in a Nitric Acid Solution

Hiroshi Ohashi, Shunji Kato and Takashi Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, **No. 86,** 45 (1978)

The dissolution of uranium dioxide, triuranium octaoxide and uranium trioxide was studied in nitric acid solutions of various concentrations at various temperatures. The dissolution rate, in general, increased in magnitude by the sequence of $UO_2 < U_3O_8 < UO_3$. Uranium dioxide obeyed a linear law in nitric acid of low concentration, while it obeyed a parabolic law at higher concentrations. If the dissolution occurred at temperatures higher than 35°C or in a solution of higher concentration than 3 N, triuranium octaoxide invariably obeyed a simple parabolic law. However, at low temperatures or at low concentrations, the dissolution proceeded through two distinct stages, which were separated by an intermediate induction period up to several hours. The first stage, in which the rate controlling step seemed to be the diffusion of a proton through the surface layer formed during the dissolution, obeyed a parabolic law. In contrast, the second stage obeyed a linear law which was interpreted by assuming a electrochemical mechanism. Finally, the dissolution of uranium trioxide obeyed a linear law, and in this case an interpretation was given on the basis of a different electrochemical mechanism. (Japanese)

Surface Polishing and Surface Composition of Fe-Cr Alloys

Masahiro Seo and Norio Sato

Corrosion Engineering (Boshoku Gijutsu),
27, 172 (1978)

The composition depth-profile of the surface of Fe-Cr alloys (5∼30% Cr) prepared with four different surface polishing treatments has been measured by simultaeous use been measured by simultaneous of argon ion sputteretching and Auger electron spectroscopy techniques. Under the condition of suputter-etching employed, essentially the same sputtering yields were obtained for ion and chromium from the alloys. Chromium-depletion was observed in the alloy surface polished with emery paper in air, while chromium-enrichment was detected in the electropolished surface. The surface whose composition is close to the bulk alloy composition was obtained by a mechanical polishing with emery paper in liquid cyclohexane. There is always a surface oxide film on the alloys and its thickness depends on the surface polishing treatments, decreasing in the following order; polishing with emery paper in air>electropolishing>polishing with emery paper in cyclochexane>polishing with alumina abrasives. The cathodic reduction of the polished surfaces always produces a chromium-enriched surface layer irrespective of the composition of the polished surfaces. (Japanese)

Chemical Shift Data in ESCA Spectra Useful for Surface Analyses

H. Kono

J. Metal Finishing Soc. Japan, **29,** 425 (1978)

Chemical shifts in ESCA spectra were measured for various compounds containing B, O, Cr, Fe, Cu, Se, Mo and Ta and tabulated. The chemical shift data for 27 elements were also cited from the literatures published during the past ten years. These data are useful for people working in the fields of metal finishing and metallurgy. (Japanese)

High Temperature Sulfurization of Stainless Steels

Keizo Nishida and Toshio Narita

Report of Project Research on Metal Corrosion,
Faculty of Engineering, Hokkaido University,
p 11, Sept. (1978)

Two kinds of stainless steels, SUS 27 (18% Cr; 8% Ni) and SUS 42 HP (25% Cr; 20% Ni) were sulfurized at 1 atm of pure sulfur vapor at 700～900°C in order to clarify the sulfide scale morphology of these steels and to compare their sulfurization kinetics with that of Fe-Cr alloys. The scales formed on the steels were examined by opticalmicroscopy, X-ray diffraction and Electron probe microanalysis. The results obtained are as follows:

1) Both steels are built of sulfide scales consisting of three layers (inner, intermediate, and outer layers). Activation energies for the formation of every layer are all the same.

2) The sulfurization of these steels is somewhat greater than that of Fe-Cr alloys containing same Cr content. This reason will be attributable to Ni involved in the steels.

3) Outer layers of both steels consist of ferrous sulfide containing Ni, Cr, and Mn, while intermediate layers consist of Cr_3S_4 and $FeCr_2S_4$ stratified phases at 800°C, but at higher temperatures than 800°C they have a single layer of Cr_3S_4 phase.

4) Inner layers are much enriched with Ni and Si, but intermediate layers have contained Ni, Mn and Fe showing similar distributions. Outer layers have flat profiles of Fe, Mn, Ni and S, but Cr has shown the distribution similar to an error function curve. (Japanese)

Recovery of Hydrogen by the Reaction Between Hydrogen Sulfide and Molten Metals

H. Kiuchi, T. Iwasaki and T. Tanaka

J. Min. Met. Inst. Japan, **94,** No. 10, 85, 479 (1978)

Hydrogen as a secondary source of energy commands worldwide attention at present, regarding its indefinite supply in the form of water, its storage and transportation characteristic which are both superior to electric power, and its wide metallurgical and chemical usage.

The decomposition reaction of H_2S to produce H_2 and S^0 for recycle can be regarded as a main step reaction in many closed thermochemical water-splitting cycles based on sulfur chemistry. For this reason, the decomposition of H_2S with molten metals was studied.

As molten metals, Pb, Sn and Bi were examined. Experiments were carried out in two ways. One is circulation and bubbling of H_2S gas into a molten metal. The other is soft blowing at the surface of the metal bath.

Conversion of H_2S to H_2 with Bi, Pb and Sn increased in that order. In soft blowing of H_2S at the surface of molten metals, the formation of a dense film of the solid sulfide hindered the reaction. Such prevention was not found in the experiment with molten Bi, owing to much larger solubility of S in Bi (1).

Generation of H_2 was accelerated by the addition of Ni or Cu. This is due to the catalytic action of dissolved Ni or Cu in the melt. Addition of Cu to Pb accelerated the reaction even in the soft blowing of H_2S at the surface of molten Pb. It was found that crystal growth of PbS was affected by the presence of Cu and powdery PbS was formed in stead of a dense film. Although the addition of Ni to Sn accelerated the generation of H_2, there was a marked tendency to cause strong adhesion of the solid sulfide onto the inner wall of the lance. (Japanese)

Reaction of Water Vapour with Metal Sulfide

R. Shibayama and T. Tanaka

Annual Report of the Asahi Glass Foundation
for the Contribution to Industrial
Technology, **31,** 169 (1978)

Reactions between steam and a matal sulfide such as Ag_2S, CaS, and ferrous sulfide were investigated within the temperature range 900–1100°K by monitoring the evolved H_2, for the purpose of hydrogen production from water. These reactions are characterized by solid products and can be classified into three types, that is, metal, oxide, and sulfate, respectively. For the reaction of CaS or Ag_2S with steam, it was concluded that generation of H_2 is due to the oxidation of S^{2-} in the sulfide phase. In ferrous sulfide, the contibution of the oxidation of Fe^{2+} to the H_2 evolution is of importance. Furthermore, it was confirmed that selective oxidation of Fe^{2+} or S^{2-} in the ferrous sulfide proceeds depending upon the extent of nonstoichiometry in ferrous sufide. It is also shown that the addition of lime to ferrous sufide results in considerable increase in H_2 concentration. (Japanese)

Effect of the Volcanic Ash Fall from Mt. Usu on the Quality of Water in Lake Toya

M. Nagayama and H. Tamura

Usu Eruption and Its Impact on Environment
Hokkaido University, p. 289 (1978)

Analyses of water in Lake Toya were made several times after the explosion of Mt. Usu. Alkalinity and pH of the water were almost unaltered compared to those measured previously. Concentrations of the other components such as Ca, Mg, Cl, SO_4 and SiO_2 also did not change appreciably. The buffer capacity of the lake water so far was very small owing to the prolonged supply of acidic water from iron sulfide mines; this was indicated from a small alkalinity value. It is suggested that the ash does not contain any soluble components, or dissolves extremely slowly. (Japanese)