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NUCLEAR REACTOR MATERIALS LABORATORY

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Dr. T. Mizuno, Dr. M. Moriya, Dr. H. Narita,
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S. Maekawa and F. Miyashita

Researches are carried out on several physico-chemical problems including corrosion.

(1) Mössbauer spectroscopic method was applied to investigate the reaction between various types, α, β and γ, of ferric oxyhydroxide and water vapor under the conditions of atmospheric pressure and temperature up to 600°C. All of the ferric oxyhydroxides changed to α-Fe_2O_3 at temperature between 300 and 350°C. In general tendency, temperature region, in which these changes occurred, was rather narrower than that of correspondent process in aerated environment.

(2) Mössbauer spectroscopic apparatus was constructed to investigate various reactions on iron and steel surfaces at high temperatures. This apparatus enabled us to measure the reaction rate and also to indentify the reaction products simultaneously. Its wide usefulness was demonstrated with several experimental results relating the oxidation of iron and the Sn-Fe reaction.

(3) A micro-computer system was developed for online processing the data of electrode impedance measurement at wide frequency range from 10^{-3} to 10^4 Hz. This system can be operated with FORTRAN, BASIC and other several computer languages. Measurements and analysis of electrode impedances were demonstrated with experimental results obtained for potentiostatically polarized Hastelloy C and zirconium in surfuric acid solution.

(4) Effect of several elements and compounds, such as cerium, iodine, uranyl salt and H_2O_2, upon the corrosion potential and the polarization characteristics of Hastelloy C was investigated in sulfuric acid solution. These elements and compounds may evolved in the dissolution process of spent nuclear fuel and also may compose redox system to stimulate corrosion of equipment made of high nickel alloys. Of these substances investigated, Ce^{4+} ion existed at relatively low concentration, such as 5×10^{-4} M or more, showed the most remarkable influence and it shifted the corrosion potential of Hastelloy C to noble potential region about 0.9 V vs. Ag-AgCl, in which over-passive dissolution may occur.

(5) Experimental studies continued on the hydrogen uptake of titanium and zirconium this year. The effect of pH on the growth rate of surface hydride layer was investigated for both metals under cathodically polarized ocnditions. By extrapolation of these observation as a function of polarized potential, the rate of hydrogen uptake at corrosion potential was estimated.

Some observation on retention behaviors of injected deuterium was also studied with hydride forming metals such as Ti, Mo and Ta.

(6) Gaseous hydrogen absorption was investigated for iron-titanium alloys, $FeTi_{1.5}$ and $FeTi_2$. Absorption and desorption isotherms were measured as a function of hydrogen pressure from 0.2 to 10 atm. From the data of temperature dependency of equilibrium pressure at the plateau region, the thermodynamic function were estimated. With mixed gas of protonium and deuterium, the degree of isotopic separation was determined after the absorption-desorption cycle.

(7) Kinetic studies of HTGR fuel particles were made in mixed solutions of nitric and hydrofluoric acid. Effect of concentrations of both components on the reaction rate and the rate law was investigated to clarify the reaction mechanism. An electroanalytical method of dissolved uranium was also investigated.

Oral Presentation

Influences of Oxygen and Others upon Hydrogen Uptake into Zirconium; T. Mizuno, T. Kurachi, T. Sato, T. Morozumi: The 5th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1979.

Identification of Iron Rust Components by Mössbauer Spectroscopy; H. Ohashi, M. Otsuka, T. Morozumi: The 14th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 1979.

Paint-coating on Metal and Its Testing Method; T. Morozumi: Short Courses on Metallic Corrosion and Its Prevention, Feb. 1979.

Adsorption of Uranium by Hydrous Titanium Oxide; T. Morozumi, H. Narita, S. Kawakatsu: The 1979 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Feb. 1979.

An Aspect on Environmental Regulation-Control of Water Pollution; T. Morozumi: Seminar on Technology for Environmental Preservation in East Iburi Area, Feb. 1979.

Corrosion Monitering by pH-Static Method; T. Morozumi: Seminar on Electrochemical Monitering of Metallic Corrosion Sponsored by the Corrosion Research Association in Hokkaido, Aug. 1979.

Influence of Molybdenum on 475°C Embrittlement of 25 Cr-Steel in Relationship between Anodic Polarization and Mössbauer Spectrum; S. Wajima, M. Otsuka, H. Ohashi, T. Morozumi, H. Sugawara: The Fall Hokkaido Section Meeting of the Japan Institute of Metals and the Iron and Steel Institute of Japan, Nov. 1979.

ELECTORCHEMISTRY LABORATORY

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

Students

H. Murayama, S. Fujita, Y. Matsumura, Y. Sera,
S. Ogi, T. Sakon, M. Masuda, N. Ono,
K. Okamura and N. Mitsui.

Surface analyses of metals and alloys by means of ellipsometry, AES, XPS and electrochemistry are being undertaken. The composition and structure of passive films formed on various iron-base alloys in aqueous solutions are investigated and the surface enrichment and depletion of alloying elements are revealed. Anodic oxide films formed on lead, titanium, and tantalum are also investigated. It is intended to study the depth composition profile, semiconductor characteristics, and optical properties. An investigation of the effect of light illumination on the dissolution of copper oxides in acid solutions is conducted. Furthermore, electrolytic hydrogen entry into iron in H_2S-containing aqueous solution is investigated to contribute to the fundamental knowledge of hydrogen sulphide cracking of steels.

Professor Sato attended the Second Japan-USSR Corrosion Seminar held 23-26 October in Tokyo to give a plenary lecture on the mechanism of anodic metal dissolution and the Second JIM International Symposium on Hydrogen in Metals held 26-29 November in Minakami with a paper on hydrogen entry into iron in H_2S-containing solutions.

Foreign visitors to this laboratory in 1979 are Professor A. T. Fromhold of Auburn University, U. S. A. as a JSPS visiting professor for six months from 13 June to 20 December, Professor M. B. Ives of McMaster University, Canada as a JSPS visiting professor on 8-31, July.

Dr. E. Fromm Max-Plank Institute, Stuttgart, West Germany on 29–30 October, Professor E. M. Matijevic of Clarkson College of Technology, U. S. A. on 1–2 December, Dr. G. Sandoz of Naval Research Chicago Branch Office, U. S. A. on 2–4 December, Dr. J. C. Scully of Leeds University, England on 2–4 December, Dr. J. P. Fidelle from France on 4–5 December, and Professor J. O'M. Bockris of Texas A & M University, U. S. A. on 1–2 December.

Oral Presentation

AES Analysis of Anodic Oxide Films on Cu; T. Iwata, M. Seo, and N. Sato: The 5th Hokkaido Section Meeting of JES, Jan. 1979.

Composition and Growth Kinetics of Anodic Oxide Films on Mo; N. Sato, M. Seo and N. Sato: *ibid.*, Jan. 1979.

Depth Composition Profile of Passive Films on Inconel 600 and Incoloy 800; M. Seo and N. Sato: The 14th Annual Meeting of the Hokkaido Corrosion Research Association: Jan. 1979.

Multiangle Ellipso-Reflectometry, Thickness Measurements of Passive Films on Nickel; T. Ohtsuka, K. E. Heusler and N. Sato: *ibid.*, Jan. 1979.

Composition Profile of PasisveFilms on Iron-Base Alloys; M. Seo: The 1st Seminar on Steel Properties of the Hokkaido Section of ISIJ, Feb., 1979.

Passive Films on Fe–5Mo Alloy in Neutral Solutions; M. Seo, Y. Matsumura and N. Sato: The 84th Meeting of JIM, Jan. 1979.

Measurements of Anodic Oxide Films by Multiangle Ellipso-Reflectometry; T. Ohtsuka, N. Sato and K. E. Heusler: The Annual Meeting of JSCE, May 1979.

Anodic Oxidation of Mo, Film Growth and Dissolution; N. Sato, M. Seo and N. Sato: *ibid.*, May 1979.

Hydrogen Absorption into Pure Iron in the Presence of H_2S; H. Murayama, M. Sakashita and N. Sato: The Hokkaido Section Meeting of JIM, May 1979.

Photoeffect on Anodic Oxidation of Pb in Sulphuric Acid; S.

Fujita, M. Sakashita and N. Sato: *ibid.*, May 1979.

AES Analysis of Solid Surfaces; M. Seo: Seminar sponsored by JIM, July 1979.

Recent Techniques of Solid Surface Analysis; N. Sato: *ibid.*, July 1979.

Analysis of Anodic Oxide Films on Fe-Mo Alloys; Y. Matsumura, M. Seo and N. Sato: The Hokkaido Branch Meeting of JCS, Aug. 1979.

Electrochemical Polarization Curves of Metals and Corrosion Technology; N. Sato: Seminar on Electrochemical Corrosion Monitoring sponsored by Hokkaido Corrosion Research Association, Aug. 1979.

Intensity-Following Ellipsometry of PassiveFilms on Iron; R. Nishimura, K. Kudo and N. Sato: The 4th International Conference on Ellipsometry (USA), Aug. 1979.

Ellipso-Reflectometry at Nickel in Sulphuric Acid Solutions; K. E. Heusler and T. Ohtsuka: International Conference on "Non-Traditional Approaches to the Study of the Solid-Electrolyte Interface", Snowman, Colorado, U. S. A., Sept. 1979.

Ellipso-Reflectometry of PasisveFilms on Nickel in Acid Solutions; T. Ohtsuka, K. E. Heusler and N. Sato: The Hokkaido Section Meeting of JIM, Nov. 1979.

Quantitative AES Analysis of Passive Films on Iron; Y. Matsumura, M. Seo and N. Sato: *ibid.*, Nov. 1979.

Effect of Temperature on the Composition of Passive Films on Stainless Steels; Y. Sera, M. Seo and N. Sato: *ibid.*, Nov. 1979.

H_2S-Catalyzed Hydrogen Absorption in Iron; H. Murayama, M. Sakashita, and N. Sato: The 2nd JIM International Symposium on Hydrogen in Metals, Nov. 1979.

Interaction between Metal Surfaces and Environments; N. Sato: Seminear on Steel Properties sponsored by the Hokkaido Branch of JIM and ISIJ, Dec. 1979.

ANALYTICAL CHEMISTRY LABORATORY

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

Students

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

Research being conducted in this laboratory is mainly concerned with anodic oxidation and cathodic deposition of metals, analysis of metal and oxide surfaces, and the chemistry of metallic ions in aqueous solutions. Dr. Takahashi returned to the laboratory in Nov. 1979 after one and half year working with Prof. Yeager at the Case Western Reserve University, Cleveland, Ohio. Dr. Tamura went on leave in January 1980 to work with Prof. Matijevic at the Clarkson College, Potsdam, N. Y. Prof. Nagayama attended the Second Japan-U. S. S. R. Seminar in Metallic Corrosion held in Tokyo in Oct. 1979 to give a one hour lecture on the formation of anodic oxide on A1 and Fe in near neutral solutions. A secondary ion mass spectrometer (SIMS) was installed in Feb. 1980, it is attached to the existing ESCA apparatus. This will make possible a more complete examination of metal surfaces.

Main subjects of the research in progress are as follows:

(1) The distribution of electrolyte anions in anodic oxide films. Films formed on Al and Fe in borate and phosphate solutions are examined using a chemical stripping technique combined with XPS analysis. Depth-profiles of BO_2^-, PO_4^{3-} and OH^- ion concentrations are being obtained as functions of anodizing time, solution pH, and applied potential.

(2) Effect of anion and Fe(III)-hydroxide on the air oxidation of

Fe^{2+} ions in near neutral solutions.

Ferrous ions can be oxidized by the air to form Fe (III)-hydroxide in solutions containing anions. Previous investigations have revealed that some anions like HPO_4^{2-}, F^- and BO_2^- accelerate the reaction while Cl^- and SO_4^{2-} retard it. The reaction product, Fe (III)-hydroxide, also influences the reaction. Attempts are being made to measure the oxidation rates for large amounts of coexisting Fe (III)-hydroxide and particular anions.

(3) Stability of oxide films.

The composition and hydration resistance of oxide films formed on Fe and Al are followed as a function of time after contact with neutral solutions containing fixed amounts of O_2 and anions. The oxide films are produced by air oxidation, or anodization in a neutral borate solution. Results obtained for iron oxide films show that CrO_4^{2-}, NO_2^-, and BO_2^- ions prevent the films from hydrating while SO_4^{2-} and Cl^- ions do not, HPO_4^{2-} ions maintain the films intact only when its concentration is below about 10^{-3} M. The research is being extended to cover the effect of concentrations of O_2 and the particular anions.

(4) Corrosion of iron in high temperature water.

The corrosion rate of iron in pure, high temperature water is measured by a polarization resistance method to examine the effects of O_2 concentration, temperature, and flow rate.

The surface oxide films produced are examined by XPS analysis. It was found that some Fe ions on top of the oxide film have a valency higher than +3 for temperatures below 150°C but at higher temperatures, above 250°C, the iron valency is almost +2.6 indicating a composition of Fe_3O_4.

Oral Presentations

The Composition of Aluminum Oxide Films Formed Anodically in a Neutral Borate Solution; S. Kobayashi, H. Konno, and M. Nagayama: The 5th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1979.

Effects of Sulfate Ions on the Air Oxidation of Ferrous Ions Coexisting with Fe (III)-hydroxide; H. Tamura, T. Hozumi, and M. Nagayama: The 1979 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Jan. 1979.

Adsorption of Zn^{2+} Ions on Fe (III)-hydroxides; K. Go, M. Oshima, H. Tamura and M. Nagayama: *ibid.*, Jan. 1979.

Studies on the Sealing of Anodic Oxide Films on Aluminum by the 'Pore-filling Method': M. Koda and M. Nagayama: The 14th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1979.

Fe (III)-hydroxide Catalysis of the Air Oxidation of Ferrous Ions —the Influence of Coexisting Anions—; H. Tamura, T. Hozumi and M. Nagayama: The 46th Annual Meeting of the Electrochem. Soc. of Japan, April 1979.

Depth Profiles of Boron Concentrations in Passive Oxide Films Formed on Iron in a Neutral Borate Solution; H. Konno and M. Nagayama: *ibid.*, April 1979.

XPS Analysis of Solid Surfaces; H. Konno: The Hokkaido Section Seminar of the Japan Institute of Metals, June 1979.

The Adsorption Behavior of Cd^{2+} Ions on Fe (III)-hydroxides; K. Go, H. Tamura and M. Nagayama: The 1979 Summer Meeting of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., Aug. 1979.

Changes in the Surface Structure of Fe (III)-hydroxides with Changes in the Preparation Condition; Y. Ikawa, H. Tamura and M. Nagayama: *ibid.*, Aug. 1979.

The Effects of Fe (III)-hydroxides and Coexisting Anions on the Air Oxidation of Ferrous Ions; T. Hozumi, H. Tamura and M. Nagayama: *ibid.*, Aug. 1979.

Distribution of Phosphate Ions in Anodic Oxide Films Formed on Aluminum in a Neutral Phosphate Solution; K. Fujimoto, K. Konno, H. Takahashi and M. Nagayama: *ibid.*, Aug. 1979.

Treatment of Laboratory Waste Water; M. Nagayama: The 1979 Annual Seminar of the Hokkaido Section of the Japan Chem. Soc., Sep. 1979.

Adsorption of Heavy Metal Ions on Fe (III)-hydroxides ; H. Tamura, K. Go and M. Nagayama : The 28th Annual Meeting of the Japan Soc. for Anal. Chem., Oct. 1979.

X ray Photoelectron Spectra of Fe (VI) Ions ; H. Konno and M. Nagayama : *ibid.*, Oct. 1979.

Nickel Cobaltic Oxide and Cobaltic Oxide Spinels as Peroxide Elimination Catalysts ; H. Takahashi, P. Bindra and E. Yeager : The 156th Electrochem Soc. Meeting, Los Angeles, Oct. 1979.

Electrochemical Behavior, Structure and Composition of Oxide Films Formed on Al and Fe in Aqueous Solutions ; The 2nd Japan-USSR Seminar on Corrosion of Metals M. Nagayama, Oct. 1979.

Chemical Composition and Dissolution Behavior of Anodic Oxide Films Formed on Aluminum in a Phosphate Solution ; H. Konno, K. Fujimoto, H. Takahashi and M. Nagayama : The 60th Meeting of the Metal Finishing Soc. Japan, Nov. 1979.

ELECTROMETALLURGY LABORATORY

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

Trust Researcher

Mr. K. Sugita

Students

H. Metoki, S. Ohkubo, M. Murakami, S. Ajimura,
T. Kawamata, K. Kasada, T. Shigematsu
and N. Yamaguchi

Research subjects in progress are as follows.

(1) Laboratory scale tests in single electrode 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 conductivity of these molten salts are being measured in this temperature range for cell design and operation analysis.

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

(3) Corrosion inhibition action of benzotriazole and its derivatives is being studied by means of electrochemical techniques. Particular emphasis is placed on the behavior of copper alloys and steels in flowing solutions in the presence and absence of the inhibitors in view of application of the inhibitors to solar heating and colling systems.

(4) Immersion tests and resistometric test for corrosion of ferrous 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 the

corrosion of pipe-line materials, some fundamental corrosion tests are being carried out under controlled conditions of vibrating.

Dr. Notoya attened the Chemical Congress of American Chemical Congress of American Chemical Society/Chemical Society of Japan held in Honolulu, Hawaii in April and presented a paper of copper corrosion inhibition with one of the collector reagents for copper oxide minerals.

Oral Presentation

Electrochemical Reduction of Chromate ion with Rotating Bipolar Electrode Cell; S. Takeda, T. Sasaki and T. Ishikawa: The 5th Hokkaido Section Meeting of Electrochemical Society of Japan, Jan., 1979.

Corrosion Inhibition of Copper with Mineral Processing Reagents; T. Notoya and T. Ishikawa: 14th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1979.

Resistometry for Determining Corrosion Rate of Metals in Low Temperature Molten Salt System. —Theory and its Applications—; H. Metoki, T. Sasaki and T. Ishikawa: *ibid.*, Jan., 1979.

Fundamental Studies for Development of Electrolytic Techniques of Aluminum Chloride; T. Ishikawa: Symposium on the Technical Aspects of Light Metal Smelting Processes, Light Metal Society of Japan, Feb., 1979.

Introduction to Metallic Corrosion and Its Prevention; T. Ishikawa: The Special Meeting of the Corrosion Research Association in Hokkaido, Feb., 1979.

Corrosion Inhibition of Copper with Potassium Octylhydroxamate; T. Notoya and T. Ishikawa: The Chemical Congress of American Chemical Society/Chemical Society of Japan in Honolulu, Hawaii, April, 1979.

Alkyl Hydroxamates as Corrosion Inhibitors for Copper and 70/30 Brasses in Sea Water; T. Notoya and T. Ishikawa: '79 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1979.

Correlation between Soluble Behavior of Metallic Aluminum and Current Efficiency in the Chloride Melts containing Aluminum Chloride; T. Ishikawa: The 18th Commitee of Fused Salt, May, 1979.

Corrosion Inhibition of Aluminum Brasses in Sea Water; T. Notoya and T. Ishikawa: The 1979 Summer Meeting of the Hokkaido Section of the Japan Chemical Society, Aug., 1979.

Corrosion Monitoring by Resistometry; T. Ishikawa: Seminar on the Electrochemical Monitor for Metallic Corrosion, The Corosion Research Association in Hokkaido, Aug., 1979.

A Novel Rotating Bipolar Electrode Cell; T. Sasaki, S. Takeda and T. Ishikawa: The 1979 Fall Meeting of Electrochemical Society of Japan, Oct., 1979.

Corrosion and Its Prevention of Ferrous Materials; T. Ishikawa: The 10th Seminar of the Hokkaido Section of the Mechanical Engineering Society of Japan, Oct., 1979.

Continuous Measurement of Corrosion Rate in Molten Salt System; H. Metoki, T. Sasaki and T. Ishikawa: The 26th Symposium on Corrosion and Prevention, The Japan Society of Corrosion Engineering, Nov., 1979.

Electrowinning of Liquid Aluminum by using Funnel Pile Type Bipolar Electrode Cell (Part 6) On the Operation of 70 A and 10 Unit Cell in Laboratory; S. Konda, T. Ishikawa, M. Kawada and K. Sugita: 13th Symposium on Molten Salt Chemistry, Nov., 1979.

Studies on the Properties of High Temperature Chloride Melts containing Aluminum Chloride (Part 3) Electric Conductivity of Various Solvent Salt System and Simple Method for its Measurement; Z. Asano, S. Konda and T. Ishikawa: *ibid.*, Nov., 1979.

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

K. Kurokawa, Y. Takeda, M. Ikeda, A. Sato, N. Suzuki,
S. Hashimura and Y. Mamiya

Our laboratory is concerened with research subjects on corrosion and protection of metallic materials at elevated temperatures as well as the related diffusion phenomena. The surface coating to improve the anti-corrosion properties of refractory metals as Ta, Nb, Mo, and V is being continuously investigated by making use of the aluminum vapor-solid diffusion couple.

The main subject is on high-temperature sulfidation of the iron based alloys in connection with coal conversion. Up to present, sulfidation of Fe–Mn alloys in pure sulfur gas environment has been completed over the whole composition range in the temperature range from 700 to 1000°C. The result is in press. The sulfur potential in corrosion atmosphere is expanding from pure sulfur vapor to low sulfur pressures, in which region only the base metal sulfide can be formed. In the systems of Fe–Cr and Fe–Mn alloys the effect of alloying elements on the sulfidation behavior of Fe in very low sulfur pressure presents a striking contrast to those in high sulfure pressure. The research on corrosion of iron and its alloy in SO_2 gas environment was devoted to elucidate the mechanism of the lamellar structure of sulfide and oxide formed on pure iron.

The fresh research program was commenced on the surface coating of stainless steels and refractory metals with borides basing on a PVD method. The first fruit was obtained for utility of the boriding on titanium sheets against corrosion in various Ar–SO_2 atmospheres at 1000°C.

Professor K. Nishida participated in the Japan-U. S. Joint Seminar on "Transport in Non-Stoichiometric Compounds", Oct. 10–12, 1979, held in Hawaii and presented the paper entitled "Sulfidation of Fe–Mn alloys under Low Sulfure Pressures". Dr. K. Godlewski, the visiting researcher from Academy of Mining and Metallurgy in Cracow, Poland, has returned to his country in March after spending his sabattical period for one year. In Oct., Dr. Narita came back from McMaster University, Canada. During his staying in Canada Dr. Narita attended the Boston Meeting of the Electrochemical Society (May, 1979), The Conference on Metal Chemistry of Canada held in Kingston (June, 1979), and Gordon Research Conference on Dry Corrosion held in New London (July, 1979).

Oral Presentations

Anticorrosion Properties of Niobium Sheets by Surface Treatments; M. Hachinohe and K. Nishida: The Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1979.

Corrosion Behavior of Pure Iron and Its Alloys in SO_2 Gas Atmosphere at Elevated Temperatures; K. Kurokawa, T. Narita and K. Nishida: The Spring Meeting of the Japan Institute of Metals, April 1979.

Anti-oxidation Properties of Calorized Tantalum Sheets at High-Temperatures; M. Hachinohe and K. Nishida: *ibid.*, April 1979.

Interdiffusion in α Phase of an Fe–Sn System; T. Yamamoto, T. Takashima and K. Nishida: *ibid.*, April 1979.

Mechanical Properties of the Sintered and Rolled Sheets of Iron Powder from the Fluidized Reduction Process; Y. Suzuki, S. Sayama and K. Nishida: The Spring Meeting of Iron and Steel Institute of Japan, April 1979.

Diffusional Analyses of the Sulfide Scale Growth on Co–Fe Alloys; Toshio Narita and Walter W. Smeltzer: The 154th Annual Meeting of J. E. C. S. (Boston), May, 1979.

High-Temperature Sulfidation of Fe–Mn Alloys in Low Sulfur

Pressures (Part II); K. Nishida and K. Godlewski: The Hokkaido Section of the Japan Institute of Metals, June, 1979.

Sulfidation Properties of an Fe-25%Cr Alloys in H_2S/H_2 Atmospheres (Part I); T. Narita and Walter W. Smeltzer: The 3rd Canadian Metal Chemistry Conference (Kingston), June, 1979.

Sulfidation Properties of an Fe-25%Cr Alloys in H_2S/H_2 Atomspheres (Part II); T. Narita and Walter W. Smeltzer: The 23rd Canadian Mining and Metallurgy Conference (Sudbury), Aug., 1979.

Interdiffusion in α Phase of a Co-Si System; T. Yamamoto, T. Takashima and K. Nishida: The Fall Meeting of Japan Institute of Metals, Oct., 1979.

High-Temperature Sulfidation of Fe-Mn Alloys in Low Sulfur Pressures (Part III); K. Nishida and K. Godlewski: *ibid.*, 1979.

High-Temperature Sulfidation of Fe-Cr Alloys in H_2S/H_2 Gas Mixtures; T. Narita, W. W. Smeltzer and K. Nishida: *ibid.*, Oct., 1979.

Study on the Sulfidation of Fe-Mn Alloys in H_2S/H_2 Gas Mixtures at Elevated Temperatures; K. Nishida and K. Godlewski: U. S.-Japan Joint Seminar on "Transport in Non-Stoichiometric Compounds", Oct., 1979.

Introductory Remarks to Interdiffusion Phenomena from Vapor Phase to Solid; K. Nishida: Symposium on the Surface Science and the Related Diffusion Phenomena, Nov., 1979.

Interdiffusion in a Ta_2O_5-Al_2O_3 System; K. Atarashiya, Y. Tsuda and K. Nishida: The Hokkaido Section Meeting of the Japan Institute of Metals, Nov., 1979.

Reduction Rate of Pulverized Hematite Containing Foreign Oxides under Hydrogen High Pressures; Y. Suzuki, S. Sayama, K. Nishida and S. Kondo: *ibid.*, Nov., 1979.

PHYSICAL METALLURGY LABORATORY

Prof. Dr. T. Takeyama, Assist. Prof. Dr. T. Shibata
Dr. H. Takahashi and Mr. M. Hachinohe

Students

S. Ohnuki, H. Ohkami, T. Yanagisawa, T. Sato,
S. Maruyama, S. Wazima, T. Ebe, T. Kato,
M. Sano and Y. Tanaka

This laboratory is mainly concerned with radiation induced damages in metals and alloys which will be used in fast breeder reactor and fusion reactor. Swelling or void formation, and radiation induced segregation in irradiated metals and alloys are pursued extensively with the aid of high voltage electron microscope and analytical electron microscope with energy dispersive x-ray analyser (EDX). Hydrogen induced blistering and cracking in ferrous alloys and pitting corrosion or stress corrosion cracking of stainless steels and titanium alloys are also investigated. Details of the research subjects in progress are as follows:

1) Radiation induced segregation has been found near grain boundary and void in electron irradiated Cu alloys. Positive or negative concentration profiles of substitutional elements near the interface can be decided by means of EDX. Positive concentration profile, that is, segregation near the interface is observed for undersize solute. Radiation induced self interstitials combined with undersize solutes are suppose to migrate to the boundary where annihilation takes place, resulting in segregation. Similar phenomena are observed for nickel alloys.

2) Effect of composition on the void swelling in electron irradiated Cu–Ni binary alloys is investigated. Alloying in solid solution by either Cu or Ni to the pure matrix metal is found invariably to supress the void swelling. These facts are rationally explained by assuming that the addition of the larger size Cu de-

creases the extent of vacancy saturation through trapping of vacancy and decrease in bias action of dislocation and the addition of the smaller size Ni accelerates the interstitial trapping.

3) Mechanical properties and structural changes of Mo at high temperatures is examined by using a ultra high temperature tensile test machine. A special device is designed for quenching the structure at a high temperature after a given extent of elongation.

4) Hydrogen induced blisters and microcracks in Fe with a small addition of carbon and titanium is studied. The fact that the addition of titanium tends to supress the formation of blister is rationally explained by the high absorption capability of titanium carbide for hydrogen.

5) Effect of impurities on the recrystallization of aluminum is examined by TEM. Impurities are found to retard the recrystallization. Etch figures of recrystallized aluminun show a characteristic change corresponding to the structural change in the bulk.

6) Stress corrosion crack velocity of titanium in iodine-methanol is determined as a function of stress intensity factor and temperature. The I and II region are observed, and a positive temperature dependence of the velocity below room temperature is found in the I region.

7) Pit generation of 17 Cr ferritic stainless steel with or without a small addition of titanium is investigated with the aid of the multichannel pitting corrosion testing apparatus which had been developed in this laboratory. With the addition of titanium, the pitting potential of the alloy shifts to the noble value, and more than two processes are found to operate during pit generation.

8) Probability distribution of stress corrosion cracking failure times of Type 316 stainless steel in boiling $MgCl_2$ solution is determined. The distribution is found to obey the Weibull distribution function. The shape parameter depends on temperature and concentration of the solution and applied stress.

In April, Prof. Takeyama and Dr. Takahashi attended the 5th International Conference on Positron Annihilation held at Lake Yamanaka, Japan, to present a paper of Study of Neutron Irradiation Damage in V and V-C Alloys by Means of Electron Microscopy and Positron Annihilation. In November, Prof. Takeyama attended the Second JIM International Symposium on Hydrogen in Metals held at Minakami, Japan, to read a paper on Formation of Micro Crack due to Hydrogen Aggregation in Iron and Steel. In October, Assist. Prof Shibata participated the Second JAPAN-USSR Corrosion Seminar held at Tokyo, to read a paper entitled Pitting Potential as a Function of Potential Sweep Velocity.

Dr. Takahashi went abroad to work with Dr. M. Wilkens, Max-Planck-Institut für Metalforschung, Institut für Physik, Stuttgart, West Germany, for radiation damage of metals by means of HVEM. He will stay with his family for about one year until October, 1980.

Oral Presentations

Observation of Initial Cracking in Hydrogen Charged Pure Iron; T. Takeyama: Symposium on Metals and Hydrogen sponsored by the Japan Institute of Metals, Nov., 1978.

Change in Mechanical Properties and Structure with Annealing of Neutron Irradiated V and V-C Alloys; H. Takahashi: Seminar on the Cooperative Research sponsored by the Research Institute for Iron, Steel and Other Materials, Tohoku University, Dec., 1978.

Irradiation Induced Segregation and Precipitation; T. Takeyama: Seminar on the Fusion Reactor Materials sponsored by the Japan Institute of Metals, Dec., 1978.

Irradiation Defects and Precipitation; T. Takeyama: Seminar on New Frontier of Ultra High Voltage Electron Microscopy in the Field of Physics and Material Research. Dec., 1978.

Stochastic Properties of Localized Corrosion; T. Shibata: The 14th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1979.

Morphology of Fine Particles in the Fallout from Usu Volcanic Eruption; T. Takeyama and G. Tomita: The Hokkaido Section Meeting of Japan Society for Electronmicroscopy, Feb., 1979.

Interaction between Irradiation Defects and Solutes affecting the Quench-Aging Phenomena of Fe-C-N Alloys; T. Takahashi and T. Takeyama: Symposium on Recent Topics of Precipitation of Carbo-Nitride in Steels sponsored by the Japan Institute of Metals, Feb., 1979.

Study of Neutron Irradiation Damages in V and V-C Alloys by Means of Electron Microscopy and Positron Annihilation; H. Takahashi: Seminar on Positron Annihilation, Feb., 1979.

Stress Corrosion cracking and Straining Electrode; T. Shibata: Meeting of Corrosion and Prevension Comittee, The Society of Materials Science, Japan, March, 1979.

Probablistic Evaluation of Localized Corrosion; T. Shibata: Meeting of Corrosion and Prevension Comittee, The Socirty of Materials Sciece, Japan, March, 1979.

Void Formation of Ni-Nb Alloys by Electron Irradiation; T. Hasegawa, H. Takahashi and T. Takeyama: The Spring Meeting of the Japan Institute of Metals, April, 1979.

Annealing Behavior of Structure and Mechanical Properties of Neutron Irradiated V and V-C Alloys; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid*, April, 1979.

Passive Films of Stainless Steels and Its Breakdown; T. Shibata: *ibid*, April, 1979.

Effect of Pretreatment Potentials on the Pit Generation of Incoloy 800; T. Shibata and T. Takeyama: *ibid*, April, 1979.

Study of Neutron Irradiation Damage in V and V-C Alloys by Means of Electron Microscopy and Positron Annihilation; T. Takeyama, H. Takahashi, M. Hasegawa, S. Ohnuki, S. Koike and H. Kayano, Fifth Int. Conf. on Positron Annihilation, April, 1979.

Observation of Micro Cracks in Hydrogen Charged Steels; T. Takeyama and H. Takahashi: The 35th Meeting of Japan Society for Electron Microscopy, May, 1979.

Probability Distribution of Stress Corrosion Cracking Failure Times of Stainless Steel; T. Shibata and T. Takeyama: Annual Conference of the Japan Society of Corrosion Engineering, May, 1979.

Effect of Precipitations on the Formation of Micro Cracks in Hydrogen Charged Iron ; H. Takahashi, S. Suzuki and T. Takeyama : The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, May, 1979.

Effect of Precipitation on the Formation of Crack due to Hydrogen in Fe-C Alloys ; T. Takeyama, H. Takahashi, T. Sato and S. Suzuki : The Fall Meeting of the Japan Institute of Metals, Oct., 1979.

Radiation Induced Segregation in Electron Irradiated Cu Alloys ; S. Ohnuki, H. Takahashi and T. Takeyama : *ibid*, Oct., 1979.

Pitting Potential as a Function of Potential Sweep Velocity ; T. Shibata and T. Takeyama : The Second JAPAN-USSR Corrosion Seminar, Oct., 1979.

Formation of Micro Crack due to Hydrogen Aggregation in Iron and Steel ; T. Takeyama and H. Takahashi : Second JIM Int. Symposium, Hydrogen in Metals, Nov., 1979.

Radiation Induced Segregation and Precipitation in Cu-Si Alloys ; S. Ohnuki and T. Takeyama : The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, Nov., 1979.

An Etching Technique for Orientation Pits of Titanium ; T. Shibata, T. Takeyama and T. Suzuki ; *ibid*, Nov., 1979.

Radiation Induced Segregation ; T. Takeyama : The Symposium on Materials for CTR, Nov., 1979.

Neutron and Electron Irradiation Effect on Fe-Mn Alloys ; T. Takeyama : Seminar on the Cooperative Research sponsored by the Research Institute for Iron, Steel and Other Materials, Tohoku University, Nov., 1979.

Construction of Ultra High Temperature Furnace and Thermal Fatigue of Molybdenum ; T. Takeyama and G. Tomita : The 5th Research Meeting on Fusion Reactor Materials, Dec., 1979.

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

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

Students

I. Nakamura, N. Tsuchida, K. Ōminami,
S. Ishikawa, N. Ōkita, Y. Tamotsu,
R. Togashi and K. Funaki

This laboratory is concerned with basic and applied reseaches on pyro- and hydrometallurgical extraction of nonferrous metals. Reseaches 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. Reaction between steam and a metal sulfide such as Ag_2S, CaS, and ferrous sulfide are being carried out within the temperature range 700°～1000°K by monitoring the evolved H_2 for the porpose 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:

$$M + H_2S = MS + H_2$$

$$MS = M + 1/2S_2(g)$$

(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 sulfide and 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) Pyrohydrolysis of metal chlorides.
This reaction has received much attention not only in the metallurgical field but also in the energy field owing to thermochemical splitting of water. Composition of gas and solid products formed during the reaction, the reaction mechanism, and systematic classification of the reactions are being examined.

(4) 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

Studies on Purification Process for Copper Electrolyte; T. Nagai, M. Kobayashi and K. Higashioka: Meeting of the Hokkaido Section, Electrochem. Soc. Japan, Jan., 1979.

Reduction of Metal Sulphates with Hydrogen; R. Shibayama K. Kaneko and T. Tanaka: The 1978 Winter Meeting, Hokkaido Section, JSAC and JCS, Feb., 1979.

Hydrogen Recovery by Sulphurization of Metal with H_2S and Metal

Reproduction from the Sulphide; H. Kiuchi, I. Nakamura and T. Tanaka: *ibid.*, Feb., 1979.

Fundamental Studies on Freeze-Melt Process for Recovery of Arsenic-Tri-Oxide (No. 2); K. Higashioka and T. Nagai: *ibid.*, Feb., 1979.

Thermochemical Decomposition of H_2S with Metal Sulphide or Metal; H. Kiuchi, T. Iwasaki, I. Nakamura and T. Tanaka: Symposia at the ACS/CSJ Chemical Congress, 1979, April, 1979.

Mechanism of Reduction of Metal Sulfate with Hydrogen; R. Shibayama and T. Tanaka: *ibid.*, April 1979.

A Study for the Effective Utilization of Hyrogen Sulphide (V); H. Kiuchi, I. Nakamura and T. Tanaka: Annual Meeting, Min. Met. Inst. Japan, April, 1979.

A Hydrometallurgical Process for Production of Arsenic-Tri-Oxide (No 2); K. Higashioka and T. Nagai: *ibid.*, April, 1979.

Sulfurization of Metal with H_2S for Hydrogen Recovery; H. Kiuchi I. Nakamura and T. Tanaka: The Hokkaido Section Meeting of JIM and ISIJ, May, 1979.

Treatment of Arsenic- Bearing Solutions at Sub-Zero Temperature; T. Nagai and K. Higashioka: Meeting of the Hokkaido Section, Min. Met. Inst. Japan, June, 1979.

Reaction of Water Vapour with Metal Chlorides; R. Shibayama N. Tsuchida and T. Tanaka: The Hokkaido Section Meeting of Min. Met. Inst. Japan, June, 1979.

A Study for Desulfurization of Metal Sulphide with Alkaline Carbonate; R. Shibayama, K. Ominami and T. Tanaka: *ibid.*, June, 1979.

A Study for Hydrogen Production from H_2S with Silver; H. Kiuchi, I. Nakamura and T. Tanaka: *ibid.*, June, 1979.

Thermochemical Splitting of H_2S by Using Solid Metal; H. Kiuchi I. Nakamura and T. Tanaka: The 1979 Summer Meeting of the Hokkaido Section of the JSAC and JCS. Aug., 1979.

Purification of Copper Electrolyte by Solvent Extraction; T. Nagai: The 11th Meeting on Electrolytic Metallurgy, "Symposium on Solvent Extraction", July, 1979.

Hydrogen Production through Sulphides; T. Tanaka, H. Kiuchi, and R. Shibayama: The 46th Meeting of the Fuel Soc. Japan, Sept., 1979.

Recovery of Hydrogen and Elemental Sulfur from Hydrogen Sulfide (III); H. Kiuchi, I. Nakamura and T. Tanaka: The Hokkaido Section Meeting of Min. Met. Inst. Japan, November, 1979.

Studies on the Pyrohydrolysis of Metal Chlorides (II); R. Shibayama, N. Tsuchida and T. Tanaka: The Hokkaido Section Meeting of Min. Met. Inst. Japan, November, 1979.

Action of Metal Sulfide on the Thermal Decomposition of Hydrogen Sulfide; H. Kiuchi, I. Nakamura and T. Tanaka: The Hokkaido Section Meeting of JIM and ISIJ, November, 1979.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

H. Ito, Y. Kawahara, M. Kitase, G. Sada,
A. Sugawara, H. Suzuki and M. Toda

In this laboratory, researches being conducted are mechanical properties and failures of engineering materials for machinery. Main subjects are concentrated on cast irons and failure analysis of machine members.

Professor Nagaoka attended the 46th International Foundry Congress, Madrid, Oct. 1979, and visited Centre Technique de la Fondrie in Paris, Department of Metallurgical and Mining Eng., University of Wisconsin in Madison and Department of Mechanical Eng., University of Alberta in Edmonton.

A book entitled the Failure Analysis of Machine Members was published by Professor Nagaoka in March 1979.

Subjects of research are as follows:

(1) Bending strength of cast iron circular plates was examined under distributed load. Non-elastic stress analysis by FEM revealed that the high nominal bending strength was attributed to both the non-elastic stress-strain behaviour of cast iron and the effect of stress gradient in the plate.

(2) Effect of circumferential ribs with various size and positions on the bending strength of cast iron circular plate was examined experimentally and theoretically. Stress analysis by FEM was valid to predict not only the effect of ribs on the strength but also the location of fracturing; at the rib, center of disk or behind the rib.

(3) The effect of specimen size and prfiles on the tensile strength

of cast iron was examined. According to the experiment, fillet radius larger than 2d (d: specimen diameter) had little effect on strength, that was confirmed theoretically by FEM stress analysis. Tensile strength was lowered by the long gauge length up to 3d, but was not lowered by specimen diameter d of 9∼18 mm. The common size-effect theory for brittle materials was not applicable to cast iron.

(4) It was tried to convert the plane distribution of graphite nodules in SG iron measured by Q. T. M. to the three dimensional distribution of them with a statistical method for calculation proposed by Saltykov. The result was applied to analyze the effect of section size and positions in castings on the distribution of graphite nodules.

(5) Changes of graphite phase due to growth in SG iron were measured by Q. T. M.. During the growth, total number and area of graphite nodules in the microstructure were progressively increased. It was analyzed that the increase was attributed to the enlarging of nodule and to the appearing of fine particle in the graphite phase.

(6) Some tests of mechanical properties were carried out on nodular and flake cast iron grown up to 10% linearly in air. As the iron grew by thermal cycling, so the tensile strength and hardness decreased progressively. The strength of nodular cast iron after the growth of 8% was about 70% of as cast one. Results of sonic test showed that the damping coefficients of nodular iron grown by 4∼6% were lowest, though the resonance frequency progressively reduced up to the growth of 10%.

(7) Recently an oxygen pump using Zirconia element has been developed to control the concentration of oxygen in gases automatically. The oxygen pump was valid to test the effect of oxygen in atmosphere on the growth characteristics of cast iron. The result on flake cast iron was almost identical to that obtained in mixed oxygen-argon gases prepared manually in the former experiments. The maximum growth rate reconfirmed was obtained in the dilute air of about 4% oxygen.

(8) Tensile creep strain of tempered martensitic steel was tested at 200°C for one hour with high-temeperature strain gauge. Steels

tempered above 300°C showed little creep strain, though those as-quenched and tempered at 200°C showed appreciable creep strain. The creep strain was dependent upon the stress applied up to 40 kgf/mm^2.

(9) Metallurgical changes due to soldering were examined on brass castings and copper tube for heat supplying use. In both of silver and brass soldering recrystallization and softening of copper tube occured markedly, though diffusion of solder metal was only in brass soldering.

Oral Presentations

Case Studies of Failure Analysis of Machine Members; K. Nagaoka: The 19th Course of Lecture by the Hokkaido Section of the Japan Society of Mechanical Engineers, Jan. 1979.

Fracture-mechanism and Strength of Metals; K. Nagaoka: The Cuorse of Lecture by the Hokkaido Section of the Japan Institute of Metals, Feb. 1979.

Rupture Strength of Circumferentially Notched Cast Iron Bar; T. Noguchi: The 28th Grand Lecture Meeting of the Society of Material Science, Japan, May 1979.

Quantitative Analysis of Graphite Phase in S. G. Iron with a Particle Analyzer; K. Miyagi, T. Noguchi and K. Nagaoka: The 95th Grand Lecture Meeting of the Japan Foundrymen's Society, May 1979.

Changes of Graphite Phases by Growth in the Ferritic S. G. Iron; M. Sōma and K. Nagaoka: The 95th Grand Lecture Meeting of the Japan Foundrymen's Society, May 1979.

FEM Analysis of Bending Strength of Cast Iron Circular Plate; T. Noguchi and K. Nagaoka: The 95th Grand Lecture Meeting of the Japan Fpundrymen's Society, May 1979.

Effects of Circumferential Rib on the Bending Strength of Cast Iron Circular Plate; T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture meeting of the Japan Foundrymen's Society, July 1979.

Analysis and Prevention of Failures of Machine Members; K.

Nagaoka: The Course of Engineering Techniques by the Press Nikkan Kogyo, July 1979.

Effect of Oxygen Concentration in Air on the Growth of Cast Iron; M. Sōma and K. Nagaoka: The 96th Grand Lecture Meeting of the Japan Foundrymen's Society, Oct. 1979.

Mechanism of Growth in Nodular Cast Iron (Castoff Void Theory); K. Nagaoka: Lecture at Metallurgical Department of Wisconsin University, Oct. 1979.

Recent Progress in Techniques of Corrosion Study

N. Sato

Metall, **33**, No. 10, 1039 (1979)., and also Proceedings
of the 7th International Congress on Metallic
Corrosion, p. 119 (1979)

The recent methodological advances in corrosion rate estimation, passivity, and stress corrosion cracking of metallic materials in aqueous environments are outlined. Critical comparison is made of three methods for electrochemical corrosion rate estimation; Tafel line extrapolation, polarization resistance, and charge transfer resistance. **In situ** and **ex situ** techniques for measuring passivity and passive films, such as ellipsometry, specular reflectrometry, photoelectric potential, electron spectrometry, ion spectrometry, membrane potential, and mechano-electrochemical techniques, are described. In stress corrosion cracking, the major advances are the fracture mechanics approach, slow strain rate tests, and acoustic emission applied for detecting SCC. (English)

The State of Understanding Metallic Passivity

N. Sato

Proceedings of the Ist Soviet-Japanese Seminar
on Corrosion and Protection on
Metals, p. 36 (1979)

Since the First International Symposium on Passivity in 1967, a considerable progress has been made in understanding the metallic passivity. This paper describes the present state of phenomenological and mechanistic understanding of the passivity of metals and alloys: 1. Anodic polarization curves, 2. Passivation processes, 3. Passive films, 4. Dissolution of passive films, and 5. Theory of passivity. It is concluded that, although many detailed problems remain to be solved, a general framework of passivity and passive films has been established. (English)

Passivity Breakdown and Pitting

N. Sato

Proceedings of the Ist Soviet-Japanese Seminar
on Corrosion and Protection on
Metals, p. 258 (1979)

Recently, passivity breaksown and localized corrosion have received much attention and ocmprehensive reviews on the recent progress in these subjects have been published. This article briefly deals with some of the key points of local passivity breakdown and pitting, a type of very localized corrosion that appears on passivated metal surface in the presence of aggressive anions. No general concepts have been established on the characterization of passivity-destroying anions but those anions which destroy the water structure tend to produce passivity breakdown. Even in the absence of aggressive anions, microbreakdown and microrepassivation are taking place in the passive film. When the intensity of passive film breakdown, which may be represented by the product of pit dissolution current density and pit size, exceeds a critical value, pitting dissolution commences to occur. (English)

Effects of Cyclic Potential-Sweep on the Electrochemical Passivation of Stainless Steels

T. Ishikawa

Proc. 7th ICMC, Vol. 1, 363 (1979)

Two current peaks can be observed in the active-passive polarization curves for stainless steels activated in deaerated acidic solutions. It has been found on these current peaks that first peak observed at less noble potential depends not only on the potential-sweep rate but on the kind of anion contained in the solution, while, second current peak at noble potential is not too much varied with the kind of anion.

In present work, the anodic currents were followed as the potential of active stainless steel was repeatedly changed to various potentials at various sweep rates in the way of sawtooth wave. Consequently, it became evident that the first peak current was reproducible to such cyclic potential-sweep regardless of sweep rate if the potential returned not to initiate secondary passivation process corresponding to the second peak current, however, the secondary process was markedly irreversible and strongly affected to the first current peak for further cyclic potential-sweep.

These behaviors of stainless steel anodically polarized would be related to stability of passive films formed with the second peak current and reactivity of passivated surfaces. The information from this paper could be provided some necessary conditions to measure the reproducible polarization curves of activated stainless steels. (English)

Passivity and the Breakdown of Passivity of Stainless Steel

G. Okamoto and T. Shibata

Passivity of Metals (Proc. 5th Int. Symposium on
Passivity), Edited by R. P. Frankenthal and
J. Kruger, The Electrochemical Soc,
INC., New Jersey, p. 646, (1978)

This review paper describes at first a brief chronological survey on the passivity studies of stainless steels, followed by the current understanding of the structure of passive films on stainless steels based on recent research efforts using various kinds of modern surface characterizing techniques, and finally the function of the film to maintain the passivity or to resist breakdown is discussed. In addition, studies on the beneficial effect of molybdenum to improve the passivity of stainless steel against chloride attack are reviewed. It is emphasized that chromium enriched in the film with incorporated bound water plays a critical role in maintaining the stable passivity which is not at rest, but "being alive" in a dynamical balance between breakdown and repair of the film. (English)

The Inhibitive Action of Bound Water in the Passive Film of Stainless Steel Against Chloride Corrosion

H. Saito, T. Shibata and G. Okamoto

Corrosion Science, **19,** No. 10, 693 (1979)

The stability of passivated 304 stainless steel specimens in the presence of chloride ions was investigated in relation to the amount of bound water in the passive film. As a measure of the stability the induction period for pit initiation and number of the anodic fluctuation prior to pit initiation were used. The amount of bound water was controlled by varying of passivation potentials, passivation times and passivation temperatures. Two kinds of bound water with different inhibitive action against corrosion by chloride ions were found in the passive film. (English)

Effect of Pretreatment Potentials on Pit Generation of Incology 800

T. Shibata and T. Takeyama

Journal of The Japan Institute of Metals,
43, No. 3, 270 (1979)

Pit generation of Incology 800 in 3.5% NaCl solution has been analysed on the basis of a stochastic theory. A parallel combination of several processes was found to be included in the pit generation at a constant potential. The number of the processes and their pit generation rates altered depending on the pretreatment potential as well as the potential applied during pit generation. The increase of the pretreatment potential caused to decrease the number of the process and also the rate of pit generation. The critical pitting potential which does not depend on the pretreatment potential and the potential sweep velocity can be determined when the pretreatment potential is more noble than −0.10 V. (Japanese)

Ellipsometric Study of Localized Metal Corrosion —Ellipsometric Spectroscopy of Passive Films on Iron—

M. Seo and H. Gotoh

Reports of the Asahi Glass Foundation For
Industrial Technology, **33**, 197 (1978)

An ellipsometric spectroscopy which can pursue rapid change in optical property of metal surface such as localized metal corrosion, has been developed by means of taking off compensator from a conventional ellipsometer and measuring directly reflected light intensity. Analyses of passive films formed on iron in neutral boric acid-sodium borate solution were made by use of this technique. The optical constants of bare iron surface and of passive films with different thickness were measured as a function of wave length (400∼700 nm). Furthermore, change in optical property of passive films due to introduction of chloride ions was tentatively measured to investigate initial step of pitting corrosion. The accuracy of the present apparatus, however was not enough to detect small change in optical property because of fluctuation of light source. The use of chopper and lock-in amplifier was proposed for further improvement of the apparatus. (Japanese)

Depth Profiles of Passive Films on Iron-Base Alloys

M. Seo and N. Sato

Proceedings of the 7th International Congress on
Metallic Corrosion, p. 176 (1979)

A differential method for obtaining the exact composition profiles in depth by use of AES and argon ion sputter-etching was applied to the analyses of Fe–30Cr alloy, 304- and 316- stainless steels potentiostatically passivated in deaerated 0.5 M sulfuric acid solution. From the measured composition profiles in depth, the surface excess of components, Γ_{Cr}, Γ_{Ni}, Γ_{O} on the dividing surface with $\Gamma_{Fe} \approx O$ was estimated as a function of anodic potential. 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. In special, the values of Γ_{Cr} and Γ_{O} on 316- stainless steel are smaller than those on 304- stainless steel, indicating that molybdenum promotes no enrichment of chromium in the passive film. The corrosion resistivity of the alloys is discussed by taking into account of both microbreakdown of the film and repassivation of the substrate alloy at breakdown sites. It is concluded that the beneficial effect of molybdenum on the corrosion resistivity can be attributed not to the stability of the film itself but to the acceleration of repassivation process at breakdown sites. (English)

Estimation of Surface Excess from Compositional Depth Profiles of Iron-Base Alloys Passivated in Sulfuric Acid Solution

M. Seo and N. Sato

Transactions of the Iron and Steel Institute
of Japan, **19,** No. 8, 505 (1979)

A differential method for obtaining the exact composition profiles in depth by use of AES and argon ion sputter-etching was applied to the analyses of Fe–30Cr alloy, 304- and 316-stainless steels potentiostatically passivated in deaerated 0.5 M sulfuric acid solution. From the measured composition profiles in depth, the surface excess of components, 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. 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. Specially, the values of Γ_{Cr} and Γ_{O} on 316-stainless steel are smaller than those on 304-stainless steel, indicating that molybdenum promotes no enrichment of chromium in the passive film. The corrosion resistivity of the alloys is discussed by taking into account of both microbreakdown of the film and repassivation of the substrate alloy at breakdown sites. It is concluded that the beneficial effect of molybdemum on the corrosion resistivity can be attributed not to the stability of the film itself but to the acceleration of repassivation process at breakdown sites. (English)

An Auger Analysis of Passive Films Formed on Fe-5Mo Alloy and Pure Iron in Neutral Aqueous Solution

M. Seo, Y. Matsumura and N. Sato

Transactions of the Japan Institute
of Metals, **20**, 503 (1979)

Composition profiles in depth of passive films on iron-5% molybdenum alloy and pure iron in pH 8.42 sodium borate-boric acid solution were measured by the combined use of Auger electron spectroscopy (AES) and argon ion sputter-etching to elucidate the role of molybdenum in the corrosion resistivity of iron-molybdenum alloys. Boron was detected in the outer layer of passive films on both iron-molybdenum alloy and pure iron but no molybdenum was detected in the outer layer of passive films on the iron-molybdenum alloy. The film thickness of the inner layer of passive films on the iron-molybdenum alloy is nearly half that on pure iron. The film thickness of the inner layer increases linearly with increasing anodic potential of film formation. The electric field in the inner layer was estimated from the slope of the linear representing the relation between film thickness and anodic potential. The estimated electric field for the iron-molybdenum alloy is about two times as high as that for pure iron. Furthermore, the diffusion coefficient of migrating ions in the inner layer was calculated from the rate equation of high field ion conduction. The calculated diffusion coefficient for iron-5% molybdenum alloy is 10^6 times as small as that for pure iron.

From these results, it was concluded that the inner layer of the passive film on iron-5% molybdenum alloy forms a barrier layer with high-resistivity against ionic conduction, which may be associated with the incorporation of molybdenum into the inner layer. (English)

Differential Composition Profiles in Depth of Thin Anodic Oxide Films on Iron-Chromium Alloy

M. Seo and N. Sato

Surface Science, **86,** 601 (1979)

A differential method for obtaining the number of component atoms in surface atomic layers is applied to the analysis of thin anodic films on Fe–30 Cr alloy surfaces in aqueous solutions. The surface excess, Γ_{Cr}, Γ_O and Γ_S on dividing surface with $\Gamma_{Fe} \approx 0$ is estimated from the measured in-depth composition profiles. The values of Γ_{Cr} and Γ_O depend on the anodic potential and the electrolyte used for the film formation. In particular, the ratio of Γ_{Cr} to Γ_O is higher in 0.5 M sulfuric acid solution than in borate solution of pH 6.48. Furthermore, the validity and usability of the present method is proved by comparing the measured values of the number density of metal atoms in the anodic oxide films with the known values of stoichiometric oxides and hydroxides of iron and chromium. (English)

Ellipso-Reflectometry Applied to the Study of Passivating Films on Nickel

T. Ohtsuka and K. E. Heusler

J. Electroanal. Chem, **100,** 319 (1979)

A method was established to derive the optical properties of a substrate and of a thin film on its surface by measuring the intensities at three directions of polarization after reflection of incident linearly polarized light. This method of ellipso-reflectometry was used to study the passivity of nickel in acid sodium sulphate solutions at pH 0.9 and pH 1.6. The optical constants of active nickel exhibited a systematic dependence on the angle of incidence and a statistical scatter related to surface roughness. Measurements with passive nickel at different angles of incidence did not provide evidence for an anisotropy of the optical constants parallel and perpendicular to the surface. The optical constants and the thickness of the passivating film depend on the electrode potential in the same way at pH 1.6, pH 0.9, and pH 0.1. The refractive index and the thickness change with the potential non-monotonously. At $E_{\mathrm{HSS}}=$ 1.05 V vs. the hydrogen electrode in the same solution, a maximum of the refractive index and a minimum of the thickness is observed, while the extinction index grows monotonously with the potential. At any constant potential, the refractive and the extinction indices both decrease with the pH value, and the thickness stays nearly constant. It is concluded that the water content of the passivating film rises with the pH value. During activation at negative potentials, the processes of reduction and transformation of the expanding film into nickel hydroxide precede the slow currentless dissolution. The first process becomes faster at more negative potentials. The dissolution rate is independent of the activation potential, is always smaller than the steady-state corrosion rate at any potential at which the film was formed prior to activation, and decreases with the pH value in the same way as the steady-state corrosion rate. (English)

Potential-Dependent Properties of the Passivating Film on Nickel in Sulphuric Acid Solution from Multiple-Angle-of-Incidence Reflectivity Measurements

T. Ohtsuka and K. E. Heusler

J. Electroanal. Chem., **102,** 175 (1979)

Relative reflectivity changes due to the formation and removal of the passivating film on nickel in 1 *M* sulphuric acid were measured at various angles of incidence. Conditions were established under which errors due to roughening by corrosion become negligible. The optical constants and the thickness of the film depend on the electrode potential. Close to the passivation potential at $U_{\mathrm{HSS}}=0.55$ V vs. the hydrogen electrode in the same solution, the refractive index is $n_2=1.9$, the extinction index $k_2=0.46$, and the thickness $d=3.15$ nm. As the potential becomes more positive, the refractive index rises to a maximum $n_2=2.3$ at $U_{\mathrm{HSS}}=1.05$ V and the thickness decreases to a minimum $d=1.7$ nm while the extinction index stays constant. At more positive potentials the refractive index increases and both the extinction index and the thickness grow larger. The results are explained by gradual hydration of nickel (II) oxide at relatively negative potentials and gradual oxidation to NiOOH at positive potentials. During activation at negative potentials two processes of film transformation and of subsequent currentless film dissolution are observed. During transformation, the refractive index decreases to $n_2=1.6$. The film becomes almost transparent and its thickness may almost double. It is concluded that transformation yields nickel (II) hydroxide. The rate of film dissolution is constant with time and of the order 0.1 nm s^{-1} to 1 nm s^{-1}. It depends on the potential of film formation. (English)

Formation and Dissolution Behavior of Anodic Oxide Films on Aluminum

M. Nagayama, H. Takahashi and M. Koda

The Journal of The Metal Finishing Society
of Japan **30**, No. 9, 438 (1979)

In this paper the authors have attempted to present a coherent picture of the present knowledge of 'anodization of aluminum' based upon the research conducted at Hokkaido University during the past fifteen years. General background for the research, and typical experimental results obtained with acidic and neutral solutions, which produce porous type and barrier type films, are described. The mechanism of film formation and its dissolution, and the composition and properties of the formed oxide are discussed with special attention to the following problems: (1) Initiation and growth of pores in the initial periods of anodizing, (2) Effect of electrical field on the dissolution of oxide, (3) Distribution of electrolyte anions in the oxide, (4) Transport of Al^{3+} and O^{2-} ions in the barrier layer during anodization. The authors demonstrate, in many aspects, that the mechanism of oxide formation is the same for both types of films, and that the porous type films are formed only in the special case where there is local dissolution of oxide, produced by the electrical field. (Japanese)

Composition and Dissolution Characteristics of Anodic Oxide Films Formed on Aluminium in Neutral Phosphate Solutions

H. Takahashi, H. Konno, T. Tamura
and M. Nagayama

Report of Project Research on Metal Corrosion,
Faculty of Engineering, Hokkaido
University, P 26, Sept. (1979)

Pure, 99.99% Al foil coupons were anodized for 10 minutes at 20°C in phosphate solutions of pHs 5.2, 7.0 and 9.3. The specimens were then transferred to a 60°C 2 M H_2SO_4 solution to dissolve the formed oxide, and the time-variations in the amounts of Al^{3+} and PO_4^{3-} ions in solution were measured. Electron microscopic examination of sections of films and the measurements of electrode impedance were also carried out. It was shown that the films have a thickness of 790±30 Å and a dielectric constant of 10.99 irrespective of the solution pH. The percentage of the phosphate incorporation in the oxide was measured to be 7.1, 6.5 and 3.0 for films formed at pHs 5.2, 7.0 and 9.3. However, phosphate was included only in the outer 600 Å portion of the films and the inner 200 Å portion was almost pure Al_2O_3. The dissolution rate of the outer layer is smaller for films formed at higher pHs probably consistent with the smaller amounts of phosphate incorporated. The inner layer dissolves at a rate slower than that for the outer layer; it was found to be independent of the solution pH. (Japanese)

A. C. Impedance of Anodically Oxidized Zirconium

T. Morozumi and M. Moriya

Corrosion Engineering (Boshoku Gijutsu)
28, No. 4, 205 (1979)

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 the A. C. signals of the current flowing between the specimen and the auxiliary electrode, as well as that of the output voltage of oscillator, were picked up with a 2ch. wave memory unit. Displayed data with a tape puncher was processed by computerized curve-fiting and calculation procedures.

At the potential region less noble than 1 V, in which the electrode process was only the growth of anodic oxide film, the impedance was almost linearly propotional to inverse frequency. In this potential region, the phase angle was almost 90° and the impedance had capacitive nature. The capacitance changed slightly with frequency in general, but a small dispersion was found nearby frequency of several or several tens Hz. The dispersion which showed a distributed relaxation time spectrum was explained with the ionic relaxation mechanism. In the potential region nearby 1.4 V, the impedance became resistive at lower frequency and it was attributed to the Faradaic process of the oxygen evolution. (Japanese)

Identification of Iron Rust Components by Thermal Changes in the Mössbauer Absorption Spectra

T. Morozumi, M. Otsuka and H. Ohashi

Corrosion Engineering (Boshoku Gijutsu),
28, No. 12, 617 (1979)

Mössbauer spectoscopy was used for the identification of the components in iron rusts formed on steel plates, nails and bolts exposed to air for long periods. The Mössbauer absorption of the rusts were measured at both room and liquid nitrogen temperatures as a function of the calcination temperature, and compared with the spectra obtained for uncalcined and calcined α-, β-, γ-, and superparamagnetic α-FeOOH. The main components of the rusts were identified as γ-FeOOH, α-Fe_2O_3, superparamagnetic α-FeOOH and superparamagnetic α-Fe_2O_3. β-FeOOH was found only in the sample exposed to a marine environment. The spectrum for magnetite, Fe_3O_4, was not obtained for any of the rusts, because sampling was made by avoiding the vicinity of the metal phase. (English)

Ion-Selectivity of Precipitate Films Affecting Passivation and Corrosion of Metals — BipolarFixed Charge-Induced Passivity

M. Sakashita and N. Sato

Proceedings of the Ist Soviet-Japanese Seminar
on Corrosion and Protection on
Metals, p. 173 (1979)

The precipitate film of corrosion products of hydrated metal oxides or other insoluble salts on the metal surface acts as solid or gel-like electrolyte in contact with corroding metals and its ion-selective properties exert a great influence on the corrosion rate of the metal. For anion-selective films the anodic current of metal Corrosion is carried by anions migrating from the solution to the metal surface giving rise to an anion enrichment and pH decrease at the metal surface. No acidification occurs at the metal surface if covered with a cation-selective corrosion product films. A bipolar film with an anion-selective layer on the metal surface and a cation-selective layer in contact with solution frequently produces the passivation of Metals. (English)

Ion Selectivity of Precipitate Films Affecting Passivation and Corrosion of Metals

M. Sakashita and N. Sato

Corrosion, **35,** No. 8, 351 (1979)

Ion selectivity in precipitate films of hydrated iron (III) and iron (III) molybdate has been studied by measuring the membrane potential and polarization property as a function of solution pH and ion valency. The hydrated iron (III) oxide membrane is found to be anion selective in 1-1 electrolyte solutions in the pH region lower than a specific pH. Beyond this pH, the membrane turns to be cation selective. This specific pH, at which the membrane potential is identical to the liquid junction potential, is named the point of iso-selectivity pH_{pis}, and is evaluated in KCl solutions to be 10.3. The hydrated iron (III) oxide membranes with adsorbed divalent anions such as MoO_4^{2-} ions are cation selective in monovalent electrolyte solutions even in the pH region lower than pH_{pis}. This cation selectivity can be attributed to the strong adsorption of the divalent anions forming the negative fixed charges on the membranes. Under an applied membrane potential, the ionic current is rectified through the bipolarized iron (III) oxide and iron (III) molybdate membranes which consist of an anion selective layer on one side and a cation selective layer on the other side. The rectification phenomenon observed in the membranes will introduce a new type of metal passivation induced by bipolarized precipitate films on metals. (English)

Effect of Precipitate Films on Metal Corrosion

M. Sakashita and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
28, No. 8, 450 (1979)

The effect of precipitate films on metal corrosion has been reviewed on the basis of the selective mass transport through the films.

Key words: cation and anion selective film, bipolar film, fixed charge, transference number, point of iso-selectivity, rectification, bipolar fixed charge induced passivity. (Japanese)

Ion-Selectivity in Hydrated Iron (II), (II•III), and (III) Oxide Precipitate Membranes

Y. Yomura, M. Sakashita and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
28, No. 2, 64 (1979)

The ion-selectivity of hydrated iron (II), (II•III) and (III) oxide precipitate membranes artificially produced on a cellulose sheet has been investigated by measuring membrane potential as a function of solution pH and ion-valency. The effect of adsorbed phosphate and molybdate anions on the ion-selectivity has also been studied. In neutral mono-monovalent electrolyte solutions, the iron (II) and (III) oxide membranes were anion-selective, and the iron (II•III) oxide membrane was cation-selective. The membranes with adsorbed phosphate and molybdate anions were all cation-selective. The fixed charge concentration and the mobility ratio of cations and anions in the membranes with and without these adsorbed anions were derived from the membrane potentials on the basis of the fixed charge theory and the thermodynamics of irreversible processes. The point of iso-selectivity pH_{pis}, above which membranes are cation-selective, was evaluated in potassium chloride solutions to be 5.8 in iron (II•III) oxide membranes and to be 10.3 in iron (III) oxide membranes. Irrespective of solution pH, the membranes were cation-selective in mono-multivalent electrolyte solutions such as sodium sulfate, and anion-selective in multi-monovalent electrolyte solutions such as barium chloride. From the ion-selective properties estimated in the precipitate membranes, discussion is presented about the local corrosion of steels underneath anion- and cation-selective precipitate films of hydrated iron oxides. (Japanese)

Corrosion Pretreatments for Copper-Zinc Alloys

G. W. Poling and T. Notoya

Corrosion, **35,** No. 1, 33 (1979)

Combinations of four different types of zinc complexing agents with benzotriazole, 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, sodium-diethyldithiocarbamate, and sodium diethyldithiophosphate, in combination with benzotrazole under a variety of test conditions.

Apart from acting as an acid inhibitor for 70/30 brass exposed to acidic NaCl solutions, the 2, 5-dimercaptothiadiazole was also an effective partner inhibitor for benzotriazole. Combinations of the other two complexing agents plus benzotriazole 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)

Effect of Pretreatment Temperature on Protection of 70/30 Brass with Benzotriazole

T. Notoya and G. W. Poling

Denki Kagaku, **47,** No. 10, 592 (1979)

Corrosion protections afforded by pretreating 70/30 brass in aqueous benzotriazole solutions at temperatures ranging from 25°C to 100°C was evaluated. Electrochemical characteristics of pretreated brass mirrors were monitored using rapid polarization technique.

Thickness of surface films were estimated by infrared multiple reflectance spectroscopy. Both corrosion current densities and corrosion rates indicated that protectiveness of benzotriazole complex films formed on 70/30 brass increased with increasing both pretreatment temperature and its period. (English)

Stress Corrosion Cracking of Titanium Alloys

T. Shibata

Bulletin of Japan Institute of Metals,
18, No. 7, 505 (1979)

Recent progress in studies on stress corrosion cracking of titanium and its alloys was reviewed. Characteristic features of the fracture surface, metallurgical and environmental factors affecting stress corrosion cracking are discussed and two alternative mechanisms, that is, mass transport kinetics model and hydrogen embrittlement theory are reviewed. (Japanese)

Electronmicroscopic Study of Micro-crack Formed by Hydrogen Precipitation in Pure Iron

H. Takahashi, T. Takeyama and T. hara

Journal of The Japan Institute of Metals,
43, No. 6, 492 (1979)

An Investigation of the nucleation sites and the structures of microvoids and microcrack formed in iron poly-crystal and single crystal in the process of the precipitation of hydrogen molecules was carried out by means of scanning and transmission electron microscopy.

Hydrogen molecules precipitated in the metal and caused it to expand to form blisters or cracks on the specimen surface during cathodic charging. The frequency of the blister nucleation was increased by the introduction of plastic strain. Besides microvoids, microcracks which were seemed to be generated as a result of the void growing were observed at greater depths in the metal membrane. In the vicinity of the microvoids, plastic deformation occurred with a consequent increase in high dislocation density and slip bands initiated from the voids along either {110} or {112} planes. Furthermore, in iron polycrystalline, microcracks were also generated at grain boundaries and the interfaces of the crack consisted of zigzag steps on {110} or {112} planes besides the interface dislocations.

The above results show that hydrogen atoms supersaturated would be preferentially absorbed on dislocations and/or grain boundary, and then microvoids and microcracks with {110} or {112} crack interface would be formed by the hydrogen precipitation as molecules. (Japanese)

Hydrogen Absorption in Cathodically Polarized Zirconium

T. Morozumi, T. Mizuno and T. Kurachi

Corrosion Engineering (Boshoku Gijutsu),
28, No. 5, 285 (1979)

The rate of hydrogen absorption in cathodically polarized zirconium was measured by using the differential etching method, in which the specimen covered with hydride was dissolved layer by layer from surface in hydrofluoric acid solution containing hydrogen peroxide, and the volume of liberated hydrogen was determined with a gas burette. Sigmoid in-depth hydrogen concentration profile was obtained with this technique and the results were ascertained both by the methods of the (d, n) reaction and the mass spectrometric measurement. Total amount of absorbed hydrogen and the thickness of hydride layer were estimated respectively by the integration of the profile and the determination of the profile front. In general tendency, the linear and the parabolic rate laws were held before and after the absorption reached at the level of 0.3 NTP cm^3/cm^2 respectively. The existence of alkaline salt in the electrolyte stimulated the absorption, and abnormally high surface hydrogen content in the hydride layer was observed. Under the condition of galvanostatically cathodic polarization the maximum absorption was obtained at $pH=7$ in any kind of electrolyte. The mechanism of absorption process was discussed on the basis of the kinetic relations among the intial rate of absorption, the electrolytic current and the electrode potential. (Japanese)

Radiation Induced Segregation

T. Takeyama

Nuclear Fusion Reactor Research, Special
Report, **42**, No. 1, 97 (1979)

This review describes recent progress in studies of irradiation induced segregation and related phenomena in metals and alloys. Enhanced nucleation by radiation induced deffects, change in free energy of irradiated material, segregation and precipitation of solute atoms migrated with radiation induced defects, and the formation of second phase are discussed. (Japanese)

Stopping Power for Deuteron in Deuterium-containing Materials

T. Mizuno and T. Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 93, 23 (1979)

The stopping power and the range of 10 to 100 keV deuterons were determined in the deuterium-containing substances, such as TiD_2, ZrD_2, PdD and D_2O. The evolution rate of neutron due to deuteron irradiation was measured as a function of the energy of the incident deuteron E_0, and the relation between them was analyzed to determine the atomic stopping cross-section S_t of the concerned atomic species by using the well-defined value of the reaction cross-cection of the (d, n) reaction. The relationship between S_t and E_0 for each atomic species was given generally by the equation $S_t = kE_0^p$, in which k was in a range from 1.20 for deuterium to 6.80 for palladium atom, and p from 0.3 to 0.4. S_t was approximately proportional to square root of the atomic number of the target atom for constant deuteron energy.

The range R was obtained by the integration of the observed inverse stopping power,

$$-\int_{E_0}^{0} (dx/dE)\, dE$$

The estimation of the local distribution of neutron evolution by using the above experimental data indicated that the main contribution to total neutron evolution was limited within a relatively small depth-range, namely approximately 40% of the deuteron range. (Japanese)

Interdiffusion in the α Phase of an Fe-Sb System

K. Nishida, H. Murohashi and T. Yamamoto
Transactions of The Japan Institute of
Metals **20,** No. 5, 269 (1979)

Iron test pieces were diffusion-annealed at 973～1223 K for 32.4～1584 ks in an evacuated quartz ampoule containing powdered (100～200 mesh) 50 wt% Sb-Fe alloy, consisting of α and ε phases, as an Sb vapor source. After annealing, cross-sections of the test pieces were analysed with an EPMA in order to determine the penetration of Sb.

Each penetration curve was analysed by the Matano-Boltzman method to calculate the interdiffusion coefficients, $\tilde{D}$. The activation energies for interdiffusion ($\tilde{Q}$) were also obtained.

The surface concentration of Sb in the test piece (α_{max}) at lower temperatures coincided approximately with solubility limit reported in the phase diagram of the Fe-Sb system, while a significant deviation in solubility limit was found at higher temperatures. Fine alumina markers placed on the test pieces prior to diffusion remained on the surface after annealing, so that it is considered that Sb atoms diffuse predominantly into the α phase of this system. Each penetration curve except for 1223 K was similar to an error function curve for a particular $\tilde{D}$ value. The value of $\tilde{D}$ showed a relatively small dependence upon the Sb concentration at each temperature. There was a gap in the Arrhenius plot of $\tilde{D}$ owing to magnetic transformation. The activation energies for interdiffusion ($\tilde{Q}$) obtained from the data at higher temperatures decreased with increasing Sb concentration from 249 kJ/mol for 1 at% Sb to 220 kJ/mol for 4 at% Sb. The activation energy for the impurity diffusion of Sb in iron (Q^*_{Sb}) was evaluated to be about 262 kJ/mol. (English)

Interdiffusion in α-Solid Solution of the Ni-Zn System

T. Yamamoto, T. Takashima and K. Nishida

Journal of the Japan Institute of Metals,
43, No. 12, 1196 (1979)

For the purpose of studying interdiffusion in an α-solid solution of the Ni-Zn system, nickel test pieces were diffusion-annealed in an evacuated capsule containing the powdered 45 wt% Zn-Ni alloy ($\alpha+\beta_1$ or $\alpha+\beta$) or the powdered 40 wt% Zn-Ni alloy (α) as a Zn vapor source at 1073∼1323 K for 3.6∼705.6 ks.

In the case of the diffusion-annealing with the former 45 wt% Zn-Ni alloy as a Zn vapor source, the surface concentration of Zn in the test piece at 1073 K coincided approximately with the solubility limit reported in the phase diagram of the Ni-Zn system, while a significant deviation toward the higher Zn concentration in the solubility limit was found at other temperatures.

For the powdered 45 wt% Zn-Ni alloy as a vapor source, fine alumina markers placed on the surface of test pieces prior to diffusion still remained on the surface after annealing, so that it is considered that Zn atoms diffuse predominantly into the α-solid solution at the marker position. For the latter vapor source used at 1323 K, the markers were found inside the test pieces after annealing. In this case, the Zn concentration at the markers position was 36.3 at% Zn and the ratio of these intrinsic diffusion coefficients in this Zn concentration, (D_{Zn}/D_{Ni}), was about 21.

The interdiffusion coefficients ($\tilde{D}$) were dependent upon Zn concentration and were evaluated to be the orders of $10^{-17}\sim10^{-13}$ m^2/s in this experimental temperature range. Log $\tilde{D}$ increased linearly with increasing Zn concentration except the case annealed at 1073 K.

The activation energies for interdiffusion ($\tilde{Q}$) obtained from these data decreased linearly with increasing Zn concentration from

265 kJ/mol for 5 at% Zn to 208 kJ/mol for 30 at % Zn. The impurity diffusion coefficient (D^*_{Zn}) at each temperature was obtained from extrapolating of $\tilde{D}$ to 0 at% Zn and the activation energy for the impurity diffusion of Zn in Ni (Q^*_{Zn}) obtained from the Arrhenius plot of D^*_{Zn} was evaluated to be 276 kJ/mol. (Japanese)

Mechanical Properties of Sintered Iron Sheets Containing Dispersed Oxide Particles

Y. Suzuki, K. Yabe, Y. Nishikawa and K. Nishida

Journal of The Iron and Steel Institute of Japan
(Tetsuo-to-Hagane) **65,** No. 2, 77 (1979)

Oxide (SiO_2 or Al_2O_3) particles were embeded to iron powder, and they were pressed, sintered at 850°C for 1 hr in a hydrogen atmosphere, roolled and annealed. The recrystallized grain size and the textures of the sheets were examined, and the relationship between these characteristics and tensile properties of the sheets were discussed.

Effects of fine oxide particles added (amorphous SiO_2 and γ-Al_2O_3: about 200 Åϕ) on the mechanical properties of the sheet were found to be remarkably high comparing with those of larger size (α-SiO_2 and α-Al_2O_3: about 2 μmϕ). In this case, the elongation decreased in general owing to fine recrystallized grain size in the matrix, although its increase appeared in the range of 0.4～0.7 vol. % addition in iron sheets. This fact suggested that the elongation was affected by the annealing texture which had been changed by additive content in the sheet.

As a result, it was found that the dispersed oxide particles and the restraint of recrystallization of the sheet by these particles improved the strength of the sheet, and exerted a major influence on the other mechanical behaviours. Moreover, it was considered that a compound was formed at the interface between iron and oxide (SiO_2 or Al_2O_3) during the sintering process. (Japanese)

Effect of Non-Uniform Stress Distribution on the Notch Strength of Cast Iron

T. Noguchi

Journal of the Society of Material Science,
Japan, **28**, No. 307, 306 (April, 1979)

In order to elucidate the effect of non-uniform stress distribution on the notch strength of cast iron, some plate specimens with edge notches or a hole were examined at room temperature and the liquid notrogen temperature. Non-elestic stress analysis was performed by FEM to discuss the fracture criterion.

The notch specimens with the elastic stress concentration factor of 1.6～5.7 ruptured at the load 5～40% smaller than the nominal stress criterion, but 8～200% larger than the maximum stress criterion. The maximum stress at the notch root was estimated as 15～80% higher than the tensile strength of the material.

These results were explained by introducting the "Boundary layer depth" δ of 2～4 mm, which was equivalent to 3～5 of graphite eutectic cells. The effect of the stress distribution decreased at the liquid nitrogen temperature where the cast iron showed almost an elastic and brittle behaviour. At that temperature, the value of δ was about 0.7 mm, which was nearly the size of an eutectic cell. (Japanese)

Failure Analysis of Machine Members

K. Nagaoka

Kogaku Tosho Co., March 1979

Machine accidents occured in industries and social activities frequently threaten human lives and facilities. In order to recover the reliability with the machine it is very important to investigate the convincing cause of accident occured unfortunately.

Failures of parts and members made of metals are followed generally on machine accident. Failure of metals are able to be analyzed theoretically with metallurgical observations and testings. However it is desirous to investigate the conditions of failure through a systematic approach, since any failure of machine member must be caused with not only metallurgical factors but also mechanical factors. In this book engineering procedures and theories for analysis of failure occured in common machine member were summarized. Furthermore many examples of failure in service and their analysis were mentioned.

Contents: Investigation of Machine Accidents/Strength and Failures of Metal/Defects of Materials/Fractography/Examination and Testings of Material/Mechanical Analysis of Failure Conditions/Procedures of Failure Investigation/Factor Analysis on Failure of Machine Members/Case Studies of Failure Analysis. (Japanese)

Purification of Copper Electrolyte by Solvent Extraction

T. Nagai

The 11th Meeting on Electrolytic Metallurgy
Symposium on Solvent Extraction,
p. 27, July, (1979)

The solvent extraction of arsenic form copper electrolyte by tri-n-buthyl phosphate (TBP) and some techniques related to replace the "Purification electrolysis" by the solvent extraction are described. Arsenate, which is major species of the arsenic in copper electrolyte, could be selectively extracted into TBP, and was stripped from TBP by water. In order to obtain As_2O_3-powder from the stripped solution, the reaction conditions to reduce the As^{5+} to As^{3+} by As_2S_3, followed by As_2O_3 recovery by "freeze-melt technique" were established. Removal of copper from the raffinate, which is required prior to nickel sulphate recovery at the subsequent step in the purification process, could be performed by hydrogen pressure reduction in an autoclave at temperature of 185°C and under hydrogen pressure of 10 atm. The addition of copper powder as "seed material" was necessary to eliminate a long induction time of the reaction. As a summary of this work, a flow sheet for purification of copper electrolyte including these techniques was suggested. (English)

The Role of Pyrophosphate in Copper Deposition from Cupric Pyrophosphate Solutions

H. Konno and M. Nagayama

Electrochimica Acta, **23**, No. 9, 1001 (1978)

Cathodic polarization characteristics of copper was examined in cupric pyrophosphate solutions of different concentrations and temperatures. The structure and composition of the deposited copper was examined by scanning electron microscopy, X-ray diffraction, electron probe microanalysis and Auger electron spectroscopy. The polarization characteristics implied that the coverage of the electrode by adsorbed pyrophosphate ions decreases with increasing cathodic polarization and it becomes almost zero past a critical potential E_b of about -0.75 V *vs sce*. E_b becomes more negative with increasing concentration of free pyrophosphate ions. As expected, pyrophosphate was incorporated at relatively high concentrations (0.05–0.07 wt% as P) in the deposits in the potential region I ($E > E_b$) and at lower concentrations (*ca.* 0.02 wt%) in region II ($E < E_b$). Smooth deposits with random crystalline orientations were obtained in a part of region I for *cd*>*ca.* 5 mA/cm^2. The rough deposits obtained outside showed preferred (220) orientations as could be expected from the orientation theory. The smooth deposition in region I is due to the pyrophosphate adsorption which inhibits the ordered deposition of copper. (English)

Correlation between Soluble Behavior of Metallic Aluminum and Current Efficiency in the Chloride Melts containing Aluminum Chloride

T. Ishikawa

YOUYUUEN (Fused Salt), **22**, No. 2, 93 (1979)

In relation to electrowinning of liquid aluminum from chloride melts containing aluminum chloride, it was observed colour changes of the melts with and without electrolytic current in a cell and followed electrochemical characteristics of the melts under oxidized and reduced conditions.

Soluble behaviors of aluminum and cathodic current efficiency were determined at 750°C in NaCl-KCl, -LiCl, -$MgCl_2$ eq. mol. solvent melts containing various amounts of aluminum chloride. According to these experimental results, some possible mechanisms on rechlorination of soluble aluminum in electrolytic cell were discussed and a desirable operating condition to save electric energy for electrowinning of liquid aluminum was proposed. (Japanese)

Current Efficiency in the Electrolysis of Aluminum Chloride

H. Ichikawa, T. Iuchi and T. Ishikawa
Light Metals 1979, Vol. 1, 363 (1979)

The reduction of aluminum chloride to aluminum has been studied with graphite electrodes in a 20 ampere cell at 750°C. Aluminum chloride gas was continuously fed to the electrolyte. The current efficiency was determined by the metal weight. Relationships between the operating and design parameters and current efficiency were found.

The following electrolysis conditions are recommended in view of energy saving: electrode angle of 30°, electrode distance of 13 to 16 mm, current density of 0.7 to 1.5 A/cm^2, and solvent composition of 20 to 30 mol. % $MgCl_2$ and/or $CaCl_2$ and 80 to 70 mol % of NaCl and/or LiCl. (English)

Mechanism of Reduction of Metal Sulfates with Hydrogen

R. Shibayama, K. Kaneko and T. Tanaka

The ACS/CSJ Chemical Congress, Symposium "Kinetics
and Mechanisms of Inorganic Reactions",
Paper 1～13, April, (1979)

An investigation on hydrogen reduction of cobalt, and copper sulfates are presented and the reduction mechanism is discussed.

The results obtained are as follows:

1) In the reduction of cobalt sulfate, metallic cobalt or Co_9S_8 is not directly formed from $CoSO_4$, but CoO is formed first, which is then reduced to metallic cobalt. On the other hand, SO_2 evolved in the course of reduction is reduced to H_2S by the catalytic action of metallic cobalt and then the H_2S formed, forms Co_9S_8. Therefore, the cyclic reaction in which the Co_9S_8 reacts with the unreacted $CoSO_4$ and forms CoO, is dominant in hydrogen reduction of $CoSO_4$.

2) In contrast to this, the conclusion is that, H_2S is not produced and only metalic cooper is obtained in the reduction of $CuSO_4$, because the lack of the catalytic action of metallic copper minimizes the formation of H_2S. (English)

Thermochemical Decomposition of H_2S with Metal Sulfides or Metals

H. Kiuchi, T. Iwasaki, I. Nakamura and T. Tanaka

The ACS/CSJ Chemical Congress, Symposium
"Requirements and Processes for Hydrogen
Generation", Paper 1~9, (1979)

The following two methods were investigated for the purpose of thermochemical decomposition of H_2S from direct reduction of sulfide ores with H_2. (1) Decomposition of H_2S by a combination of the following two reactions in which M denotes a metal; sulfurization ($MS+xH_2S=MS_{1+x}+xH_2$) and thermal decomposition ($MS_{1+x}=MS+xS$). It was found that the utilization of non-stoichiometric composition of berthollide sulfides such as FeS_{1+x} is suitable for the above cycle. Better results were obtained by using a double sulfide $CuFeS_{2-x}$ which thermally decomposed into FeS and Cu_5FeS_4 under reduced pressure and these products were proved to return to their original state $CuFeS_{2-x}$ by sulfurization with H_2S. (2) Decomposition of H_2S by metals. As a fusible metal, molten Pb was used to prevent the formation of a dense film which tends to cease the generation of H_2. Two tests were made, in which the bubbling of H_2S into molten Pb and the soft blowing at the surface of the melt were examined. Experimental results revealed that the presence of minute Ni or Cu in molten Pb serves to catalyze the formation of H_2. It was also shown that the Pb regeneration is possible by the oxidation of the formed PbS under low partial pressure of O_2 and the this regeneration is due to the reaction of sublimated PbS. (English)

Reaction of Water Vapour with Metal Sulfide (II)

R. Shibayama and T. Tanaka

Reports of the Asahi Glass Foundation for Industrial
Technology, **33**, 273~286, (1978)

Selective oxidation of iron in chalcopyrite with steam and the dissolution kinetics of magnetite with hydrochloric acid were studied in order to recover hydrogen together with copper, iron and elemental sulfur from copper sulfide ores. The reaction of steam with chalcopyrite resulted in the formation of a porous shell of Fe_3O_4 surrounding an unreacted core of the sulfide. Chalcopyrite was at first converted to a nonstoichiometric bornite and then to $Cu_{2-x}S$. Selective oxidation of iron was enhanced by the presence of CaO and the reaction was controlled by gas diffusion in the porous magnetite layer.

In the dissolution of magnetite in hydrochloric acid, the reaction rate was chemically controlled and increased with increasing ferrous ion concentration in solution. Effect of the addition of ferric ion upon the dissolution rate was not observed. (Japanese)

Measurement of Active Site Density on a Sulfided Nickel Catalyst

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J. Res. Inst. Catalysis, Hokkaido Univ.,
26, No. 2, 101 (1978)

Sulfided nickel catalysts prepared in a low pressure H_2S atmosphere at 300°C indicate the existence of three types of active sites, A, B, and C, where the degrees of coordinative unsaturation of nickel are 1, 2 and 3, respectively. The amount of adsorption of CO on the catalyst has been measured during the hydrogenation of acetylene with a H_2-CO mixture. It was found that CO adsorbs on all the sites at pressures above 5 torr, but below 1 torr the adsorption occurs only on type C sites. The upper bounds of the density of A, B and C type sites are estimated to be 2.9×10^{14}, 1.5×10^{14} and $6.4 \times 10^{13}\ \mathrm{cm}^{-2}$, respectively. (English)

On the Preparation of Large Single Crystals of Ferrous Sulfide

K. Nishida, T. Narita and M. Yamada

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 95, 129 (1979)

Some experiments for the formation of single ferrous sulfide crystals (about 1.5 cm × 1.0 cmϕ) having stoichiometric and congrent compositions (FeS and $Fe_{0.934}S$) were carried out by the Bridgeman method. The crystals obtained were examined by X-ray diffraction, optical and polarized light microscopy, and their orientations were determined by the pole figure method. The best sound crystal can be obtained by the sulfide having a congruent composition with a lowering rate of 0.33 cm/h produced in a vertical electric furnace and maintained at the highest-temperature part ($\geq$1200°C). Its crystal orientation had a (100) plane perpendicular to the crystal growth direction. (English)

Morphology of Fine Particles in the Fallout from Usu Volcanic Eruption

T. Takeyama and G. Tomita

Usu Eruption and Its Impact on Environment,
Hokkaido University, p. 65. (1978)

Fine particles in the fallout of Usu volcanic eruption are collected at Sapporo City and their morphology and chemical composition are examined by a transmission or scanning electron-microscopy as well as a microanalysis using energy dispersive X-ray technique. A thin flake shape is observed for most of particles examined, the composition of which is found to be mainly consisted of Si, Al, and Fe in addition to a small amount of Mg, K, and Mn. Sizes of particles are scattered widely, but their distribution under the size of 1.5 μm can be described as a logarithmic normal distribution. (Japanese)