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ANALYTICAL CHEMISTRY LABORATORY

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

Students

M. Koda, M. Oshima, K. Go, M. Kawai, T. Tamura
Y. Ikawa (Miss) and Y. Shibata

Research being conducted in this laboratory is concerned with anodic oxidation of metals, cathodic deposition of metals, X-ray photoelectron spectroscopy for metal surfaces and chemistry of metallic ions in aqueous solutions. Nagayama attended the 4th International Conference on Passivity held in Airlie, Virginia, in October in 1977. After the conference he was invited to the Division of Chemistry, National Research Council of Canada and Cleveland Section of the Electrochemical Society to give a talk on 'Anodizing of Aluminum'.

Topics of our research conducted during the passed one year are :

(1) Formation of 'barrier-type' anodic oxide films on Al. Oxide films were anodically formed in neutral phosphate solutions of different pHs. The phosphate concentration profiled in depth direction were examined by stripping the films in a sulfuric acid solution and measuring the amounts of dissolved Al^{3+} amd PO_4^{3-} ions.

(2) Transport numbers for Al^{3+} and O^{2-} ions in the oxide during the 'pore-filling'. Aluminium specimens covered with porous anodic oxide films were re-anodized in a neutral boric acid-borate solution at a constant c. d. Oxide formation occurs both at the barrier layer/solution and oxide/metal interfaces, corresponding to the migration of Al^{3+} and O^{2-} ions through the barrier layer. The transport numbers of these ions were determined from the porosity

of the original oxide estimated by electron microscopy and the amount of electricity required to fill up the pores in the re-anodization experiment.

(3) Dissolution characteristics of Fe (III) hydroxide. Fe (III) hydroxides were formed by adding various kinds of alkalis to a ferric nitrate solution and they were aged at various pHs and temperatures. The dissolution behavior of the hydroxides in a tartaric acid solution was examined and the results obtained were interpreted in terms of the size, density and composition of the hydroxide particles.

(4) XPS studies on metal surfaces. X-ray photoelectron spectroscopy was applied to investigate the passive oxide films formed on iron in a neutral boric acid-borate solution. The passive oxide was essentially composed of $Fe_2O_3 + FeOOH$ ($OH/Fe = 0.3 - 0.5$) and some of Fe ions had valency higher than $+3$. The same technique was applied to clarify the composition of chromic-chromate films formed on Pt during chromium plating from a chromic acid solution.

Oral Presentations

Formation behavior of anodic oxide films on aluminum in neutral solutions ; H. Takahashi and M. Nagayama : The 6th Meeting of the Hokkaido Section of the Japan Electrochemical Soc., Jan. 1977.

Properties of porous anodic oxide films formed on aluminum in a solution of H_2SO_4 containing $H_2C_2O_4$; H. Takahashi and M. Nagayama : The 1977 Winter Meeting of the Hokkaido Sections of the Jap. Soc. for Anal. Chem. and the Japan Chem. Soc., Feb. 1977.

Analysis of Fe (III) by the ferron method —Application to the study of the hydrolysis of Fe^{3+} ions ; H. Tamura, Y. Sato and M. Nagayama : *ibid.*, Feb. 1977.

Catalytic behavior of $Fe(OH)_3$ in the air-oxidation of Fe^{2+} ions—Effect of aging of $Fe(OH)_3$; H. Tamura and M. Nagayama : The 44th Annual Meeting of the Japan Electrochemical Soc., Apr. 1977.

Anodization of aluminum in neutral borate solutions; H. Takahashi and M. nagayama: *ibid.*, Apr. 1977.

Effect of cathodic pretreatment on the passivation of iron in a neutral borate solution; A. Rauscher, H. Konno and M. Nagayama: *ibid.*, Apr. 1977.

Composition of passive films formed on iron in a neutral borate solution; H. Konno and M. Nagayama: *ibid.*, Apr. 1977.

Anodization of aluminum in neutral phosphate solutions; H. Takahashi, M. Takimoto and M. Nagayama: The 55th Meeting of the Japan Metal Finishing Soc., May 1977.

Properties of anodic oxide films on aluminum; M. Nagayama: Seminor sponsored by the Hokkaido Section of the Japan Society for Precision Engineering, June, 1977.

On the factors controlling the acid dissolution characteristics of Fe (III) hydroxides; M. Oshima, H. Tamura and M. Nagayama: The 1977 Summer Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., July, 1977.

A simultaneous removal of various heavy metal ions from laboratory waste water; S. Emi, N. Kameda, H. Tamura. H. Konno and M. Nagayama: The 56th Meeting of the Japan Metal Finishing Soc., Sep. 1977.

Transport of ions in the barrier layer of the anodic oxide films on aluminum during anodizing in sulfuric acid and oxalic acid solutions; M. Koda, H. Takahashi and M. Nagayama: *ibid.*, Sep. 1977.

XPS studies on anodic oxide films formed on iron in a boric acid-borate solution; H. Konno and M. Nagayama: The 4th Intern. Conf. on Passivity, Airlie, Virginia, Oct. 1977.

Determination of porosity of anodic oxide on aluminium; M. Nagayama: Invited Lecture at National Research Council of Canada, Ottawa, Oct. 1977.

Transport of Al^{3+} and O^{2-} ions during formation of anodic oxide films on aluminium; M. Nagayama: Invited Lecture at the Cleveland Branch of the Electrochem. Soc., Cleveland, Nov. 1977.

ELECTROCHEMISTRY LABORATORY

Professor Dr. N. Sato, Assistant Professor Dr. M. Seo,
Dr. M. Sakashita, Mr. R. Nishimura
and Miss C. Mirua

Students

Y. Yomura, I. Iwata, N. Sato, H. Gotoh, H. Murayama,
S. Fujita, Y. Shin, and T. Yui

Main subjects of research in this laboratory are concerned with electrochemistry of iron-group metals and alloys. Rotating ring-disc electrodes are being used for the study of anion effect on anodic dissolution and passivation of iron and nickel. Also, detailed information of the structure and composition of anodic oxide films on molybdenum and copper has been colloected by a variety of analytical techniques such as cathodic reduction, ellipsometry, and Auger electron spectroscopy. Furthermore, a quantitative method for obtaining exact composition profiles in depth of solid surfaces has been developed and applied to analyses of anodic oxide films on iron-base and nickel-base alloys in solutions of pH ranging from acid to base. Besides, polarization curves of high tension steels in acetic acid-sodium acetate solution containing hydrogen sulfide have been measured with reference to stress corrosion cracking of steels. Moreover, studies on the ionic rectification of bipolar membranes are being conducted to reveal the role of hydrous metal oxide films formed as a corrosion porduct in producing passivity.

In July and August, Professor Sato was invited by the Organization of American States to visit five countries in Latin America. First, he was invited to lecture on the passivity of metals for two weeks from 4 to 15 July in a ten-week postdoctoral seminar on corrosion held at Comision Nacional de Energia Atomica (Dr. R. Galvele) in Buenos Aires, Argentina. After the lecture, he visited Instituto de Investigaciones Fisicoquimicas Teoricasy Aplicadas (Professor A. J. Arivia) in the National University of La Plata, Argentina, giving two lectures on the passivity of nickel and cobalt and the ion-selectivity of hydrous metal oxide membranes. Then, he moved to Conception, Chile, visiting Universidad de Concepcion CASILLA (Professor A. Pagliero), Empresa Nacional de Petroleos, and Comparna de Aceros del Pacific. In Chile, he also visited IDIEN (Dr. B. G. Joseph) Universidad de Chile, Santiago, giving a lecture on the corrosion of metals. Further, Professor Sato visited the following Universities and Institutions: 1) COPPE (Professor L. R. Miranda) in Universidad Federal de Rio de Janeiro, Brasil, 2) Centro de Pesquisase Desenvolvimento (Dr. A. C. Dutra) in RETROBRAS, Rio de Janeiro, Brasil, where he gave a lecture on the metal passivity, 3) Instituto de Investigaciones Technologicas (Dr. A. McCormick), Bogota, Colombia, 4) Instituto de Investigaciones Metalurgicas (Professor J. L. Olivars) in Universidad Simon Bolivar, Caracas, Venezuela, 5) Insituto Venezolano de Investigaciones Cientificas, Caracas, where he also lecture on the corrosion of metals.

In September, Professor Sato and Dr. Sakashita attended the 26th International Congress of Pure and Applied Chemistry held in Tokyo, presenting a paper on the ion-selectivity of corrosion product films.

In October, Professor Sato participated in the 4th International Symposium on Passivity held at Airlie House Conference Centre, Warrenton, Virginia, USA, and presents an overview paper on the passivity of metals and a contributed paper of bipolar fixed charge-induced passivity.

In December, Professor Sato visited Moscow to attend the first Japan-USSR Corrosion Seminar and presented an overview paper on metallic passivity and two contributed papers on passivity breakdown and pitting and on bipolar fixed charge-induced passivity. After the seminar, he and other eight Japanese delegates visited the following institutions to see a number of corrosion scientists and engineers in the USSR; 1) Leningrad Politechnic Institute, 2) Karpov Institute of Physical Chemistry, Moscow, 3) Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow,

4) Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow, 5) Central Institute of Iron and Steels, Moscow.

Three foreign scientists visited this laboratory: Dr. J. B. Lumsden (Department of Metallurgical Eng., The Ohio State University, Columbus, Ohio, USA) from 31 January to 3 Feburary, Dr. K. D. Christopher (Research & Development Lab., United Chemi-Con Inc., Mass., USA) on 24 June, and Dr. E. C. Potter (Mineral Research Lab., Common Wealth Scientific and Industrial Research Organization, NSW, Australia) on 19–22 August.

Oral Presentations

Auger Analysis of Anodic Oxide Films on 55Fe–45Ni Alloy in Boric Acid-Sodium Borate Solution; M. Seo and N. Sato: Annual Meeting of the Corrosion Research Association and of the Japan Electrochemical Society in Hokkaido, Jan., 1977.

Passive Films on Iron in Borate Solution and Phosphate Solution; R. Nishimura and N. Sato: *ibid.*, Jan., 1977.

Effect of pH and Ion-Valency on Fixed Charge of Hydrous Metal Oxide Membrane; M. Sakashita and N. Sato: *ibid.*, Jan., 1977.

Composition Profiles in Depth of Anodic Oxide Films on 55Fe–45Ni Alloy; M. Seo and N. Sato: Spring Meeting of the Japan Institute of Metals, Apr., 1977.

Auger Electron Spectroscopic Analysis of Passive Films on Iron; R. Nishimura, M. Seo and N. Sato: 44th Annual Conference of the Japan Electrochemical Society, Apr., 1977.

Ionic Rectification of Precipitated Membrane as a Corrosion Product; M. Sakashita and N. Sato: 4th Annual Conference of the Japan Society of Corrosion Engineering, May, 1977.

Auger Analysis of Anodic Oxide Films on Fe–Cr and Fe–Ni Alloys; M. Seo and N. Sato: *ibid.*, May, 1977.

Polarization Characteristics of Molybdenum Electrode; N. Sato, R. Nishimura and N. Sato: Hokkaido Section Meeting of the Japan Institute of Metals, June, 1977.

Auger Analysis of Chromate Films on Iron; H. Goto, M. Seo and N. Sato: *ibid.*, June, 1977.

Selective Ion Permeability of Precipitated Hydrous Iron Oxide (II, III) Membranes; Y. Yomura, M. Sakashita and N. Sato: *ibid.*, June, 1977.

Recent Trend in Corrosion Science and Technology of Steels; N. Sato: Hokkaido Section Seminar of the Japan Mechanical Society, June, 1977.

Ion-Selectivity in Corrosion Product Membranes —Fixed Charge on Hydrous Iron (II) Oxide; M. Sakashita and N. Sato: 26th International Congerss of Pure and Applied Chemistry, Tokyo, Sept., 1977.

Composition of Passive Films Formed by Two Step Oxidation on Iron in Neutral Solutions; R. Nishimura and N. Sato: 56th Meeting of the Japan Metal Finishing Society, Sept., 1977.

The Passivity of Metals and Passivating Films; N. Sato: The 4th International Symposium on Passivity, Virginia, USA, Oct., 1977.

Bipolar Fixed Charge-Induced Passivity; M. Sakashita and N. Sato: *ibid.*, Oct., 1977.

Ion Selective Permeability of Precipitated Hydrous Iron Oxide (III) Membrane —Point of Iso-selectivity pH_{pis}—; M. Sakashita and N. Sato: 30th Discussion Meeting of Colloid and Interface Science in the Japan Chemical Society, Oct., 1977.

Anodic Oxidation of Copper in Borate Solution; T. Iwata, R. Nishimura and N. Sato: Fall Meeting of Hokkaido Section of the Japan Institute of Metals, Nov., 1977.

The State of Understanding of Passivity of Iron and Iron Base Alloys; N. Sato: Japan-USSR Seminar on Corrosion Science, Moscow, USSR, Dec., 1977.

Bipolar Fixed Charge-Induced Passivity; M. Sakashita and N. Sato: *ibid.*, Dec., 1977.

Passivity Breakdown and Pitting; N. Sato: *ibid.*, Dec., 1977.

VACUUM SCIENCE LABORATORY

Prof. Dr. T. Yamashina, Assi. Prof. Mr. K. Watanabe,
Dr. M. Mohri, Dr. S. Tanaka, Mr. M. Hashiba
and Mrs. Y. Hirohata

Students

M. Yabumoto, H. Kakibayashi, K. Nakamura, M. Nishino,
S. Itoh, T. Obata, S. Kato and H. Yagami

In this laboratory, research work on the surface phenomena of solids and vacuum engineering is in progress with the following subjects :

(1) Surface study of nuclear fusion materials as the first wall of CTR : Plasma and first wall interactions have been investigated extensively, especially on the erosion phenomena of carbon and SiC surfaces by energetic protons and deuterons by means of AES-SIMS (IMA)-FDS combined systems.

(2) Selective sputtering of binary alloys : Selective sputtering processes of binary alloys such as Cu-Ni and Au-Ag are studied by a quantitative Auger spectroscopy utilizing the difference in the escape depth of Auger electrons with different energies.

(3) Surface passivation of semiconductor device : In-depth profiles of passivated films and interface of oxide-metal on GaAs are compared with those of various oxide films prepared by anodic, thermal and plasma oxidations.

(4) Adsorption and sorption of hydrogen to titanium : Kinetic and sturctural measurements of titanium-hydrogen at high temperatures are being made by means of an ultrahigh vacuum microbalance with high sensibility and a neutron scattering technique.

Oral Presentations

Simultaneous Measurement of Surface Reactions by AES-SIMS-FDS Combined System ; H. Kakibayashi, M. Mohri, K. Watanabe and T. Yamashina: The 1977 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Feb., 1977.

Titanium-hydrides by High Pressure Sorption and Its Reactivity; M. Sasaki, E. Uyeda, S. Uyeda, K. Watanabe and T. Yamashina: *ibid.*

Development of Catalytic Pump for Hydrogen; K. Nakamura, M. Hashiba, K. Watanabe and T. Yamashina: Anual Meeting Hokkaido Sections of the Japan Society of Applied Physics, Feb., 1977.

Preparation of Oxide Films of Ti-Mo by Reactive-co-sputtering; Y. Saito, Y. Hirohata, M. Mohri, K. Watanabe and T. Yamashina: *ibid.*

Chemical Structure of Passivation Films over GaAs; M. Nishino, Y. Hirohata, M. Hashiba K. Watanabe and T. Yamashina: *ibid.*

In-depth Profil of Passivation Layers over GaAs by means of AES-SIMS (III)-A Comparison of Passivation Layers Prepared by Various Methods; M. Hashiba, M. Nishino, Y. Hirohata, K. Watanabe and T. Yamashina: The 24th Annual Meeting of Japan Society of Applied Physic; Mar., 1977.

In-depth Profile of Passivation Layers over GaAs by means of AES-SIMS (IV)-A Quantitative Analysis of Interface of Oxide-Metal; K. Watanabe, M. Hashiba, M. Nishino and T. Yamashina: *ibid.*

SIMS-FDS-AES Study of Surface Reaction-DCOOH over Ni; M. Mohri, H. Kakibayashi, K. Watanabe and T. Yamashina: *ibid.*

Evaluation of Passivation Layers over GaAs by AES-SIMS; T. Yamashina: *ibid.*

Simultaneous Measurement of Surface Reactions over Metals by AES-SIMS-FDS Combined System; T. Yamashina: The 80th Annual Meeting of Japan Institute of Metals; Apr., 1977.

Quantitative In-depth Profile of Passivated Oxide Layers of GaAs by AES-SIMS-A Comparison of Thermal, Anodic and Plasma Oxidations; K. Watanabe, M. Hashiba and T. Yamashina:

Conference on Solid State Devices; Aug., 1977.

Surface Phenomena of First Wall of Nuclear Fusion Reactor (I)-Interactions of C, SiC and H^+ (D^+) with 5-15 KeV by AES-IMA; T. Yamashina, M. Mohri, K. Watanabe, H. Doi and K. Hayakawa: Annual Meeting of the Atomic Energy Society of Japan Oct., 1977.

Surface Phenomena of First Wall of Nuclear Fusion Reactor (II)-Interaction of C, SiC and Atomical Hydrogen; K. Nakamura, M. Mohri, K. Watanabe and T. Yamashina, *ibid.*

Surface Phenomena of First Wall of Nuclear Fusion Reactor (III)-Surface Area Measurement of Mo, C and SiC Irradiated with D^+ (100 KeV); M. Sasaki, H. Yagami, Y. Hirohata, M. Mohri, K. Watanabe and T. Yamashina, *ibid.*

Surface Phenomena of First Wall of Nuclear Fusion Reactor (IV)-M. Mohri, R. Obata, Y. Hirohata, K. Watanabe and T. Yamashina, *ibid.*

In-depth Profile of Clean Surface of Cu-Ni Alloys (III)-Analysis of Altered Layers Formed by Selective Sputtering; K. Watanabe M. Hashiba, H. Kakibayashi M. Mohri and T. Yamashina: The 38th Meeting of Japan. Society of Applied Physics: Oct. 1977.

Selective Sputtering and Segregation of Clean Surface of Au-Ag Alloys; M. Yabumoto, M. Mohri, K. Watanabe and T. Yamashina, *ibid.*

Evaluation of Surface Properties of SiC by means of AES-IMA Combined System; T. Yamashina, M. Mohri, K. Watanabe, H. Doi and K. Hayakawa, *ibid.*

Anodic Oxidation of GaAs in Oxygen Plasma (III)-In-depth Profile by AES-SIMS; M. Hashiba, M. Nishino, Y. Hirohata and T. Yamashina, *ibid.*

Quantitative In-depth Profile of GaAs Passivation Layers by AES-SIMS; M. Nishino, M. Hashiba, Y. Hirohata, K. Watanabe and T. Yamashina: The 18th Meeting on Vacuum Sciences; Nov., 1977.

Selective Sputtering of Clean Surface of Cu-Ni Alloys by AES-

SIMS; H. Kakibayashi, M. Mohri, K. Watanabe and T. Yamashina, *ibid.*

Surface Properties of C and SiC as First Wall Materials; K. Nakamura, Y. Hirohata, M. Mohri, K. Watanabe and T. Yamashina, *ibid.*

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

S. Okazaki, H. Senzaki, S. Karasawa, K. Sakurai
N. Kiyohara, T. Shibata, K. Miyazaki
and T. Nishizawa

The laboratory is investigating the dry corrosion of metals and alloys. The diffusions in metals and in some cermics are also being investigated on the basis of corrosion and protection researches. At present the research is being carried out on the followings:

(1) Oxidation of Co-based Mn and Mo alloys; The effect of the oxygen pressure on oxidation rates was further studied for other kinds of Co-based alloys and the composition profile in the oxide solid solutions, (Co, Me) O, was obtained.

(2) Oxidation of metallized refractory metals; Calorized Ta sheets were oxidized in air flow at 1100°C for a long lime (1000 and 3300 mins) and the change in sectional structure was examined. Further V metal sheet were metallized with a pack cementation technique in variable conditions and its protection was examined.

(3) Interdiffusion in Ni-Al and Co-Al systems; Ni and Co metal sheets were exposed to Al vapor to obtain mutual diffusion coefficients in their intermediate phases by using the vapor prepared from the two-phase powder. The data obtained were examined by comparing with the selfdiffusivity of Ni in the system and impurity diffusion coefficient of Al in Co metal was obtained.

(4) Interdiffusion in the α phase of a Cu-Zn system was examined by using Zn vapor obtained by β phase thin ribbons. The interdiffusivity ranged over a whole range of α phase of this system and it was found that the data were more accurate than those

obtained by Balluffi. Next, the homogenization of the alloy layers formed by diffusion was examined by using the diffusion theory of such phenomenon and a good agreement between calcu- lated and observed concentration profiles was obtained.

Oral Presentations

Study on Antioxidation of Ta Metal-Synthesis of Ta Oxides Containing Al, Cr and Si and Their Electric Resistance ; K. Taniguchi, T. Narita and K. Nishida : The 12th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1977 and the 3rd Hokkaido Section Meeting of Electro Chemical Society of Japan.

Study on High-Temperature Surface Chemistry of Metals and Alloys ; K. Nishida (Tanikawa and Harris award lecture) The Spring Meeting of the Japan Institute of Metals, April, 1977.

Simulation of high Temperature Oxidation of Co-Ni alloys by using an Electronic Calculator ; T. Narita and Nishida : *ibid.*, April, 1977.

Interdiffusion in the α Solid Solution of a Co-Zn System ; T. Yamamoto, T. Takashima and K. Nishida : *ibid.*, April, 1977.

Phase Equilibrium in a Ta_2O_5-SiO_2 System in the Temperature Range from 1400 to 1600°C ; K. Atarashiya, Y. Iwami, T. Narita and K. Nishida : The Hokkaido Section Meeting of JIM and ISIJ, June, 1977.

High Temperature Oxidation of Co-based Mn and Cu Alloys ; S. Karasawa, T. Narita and K. Nishida : *ibid.*, June, 1977.

The Study on Anti-Oxidation Property of V Metal (Part 1) ; K. Sakurai, T. Narita and K. Nishida : *ibid.*, June, 1977.

High Temperature Oxidation Behavior of Calorized Ta Sheets ; M. Hachinohe and K. Nishida : The 56th Meeting of the Metal Finishing Society, Sept., 1977.

Some Experiments on the Crystal Synthesis from Molten Iron Sulfide ; M. Yamada, T. Narita and K. Nishida : The Fall Meeting of Japan Institute of Metals, Oct., 1977.

High Temperature Oxidation of Co-based Alloys ; T. Narita and

K. Nishida: *ibid.*, Oct., 1977.

Interdiffusion in the α phase of a Co–Al system; S. Okazaki, T. Narita and K. Nishida: *ibid.*, Oct., 1977.

Multi-Phase Diffusion in a Ni–Al System by means of Al Vapor; H. Senzaki, T. Narita and K. Nishida: *ibid.*, Oct., 1977.

Interdiffusion in β phase of an Fe–Sb System; T. Yamamoto, T. Takashima and K. Nishida: *ibid.*, Oct., 1977.

Mechanical Properties of Rolled Iron Plate made from Sintering of Iron Powder containing some Oxides; Y. Suzuki and K. Nishida: The Fall Meeting of Iron and Steel Inst. of Japan, Oct., 1977.

Interdiffusion in an α phase of a Cu–Zn System by use of Zn Vapor; K. Sakurai, S. Karasawa, T. Narita and K. Nishida: The Hokkaido Section Meeting of JIM and ISIJ, Nov., 1977.

Formation of Dispersed Magnesia and its Hydration Reaction; K. Atarashiya: *ibid.*, Nov., 1977.

On the Cracking and Sintering of Powdered Iron Ore During Reduction in Hydrogen; Y. Suzuki, Y. Nishikawa, S. Sayama and K. Nishida: *ibid.*, Nov., 1977.

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

H. Narita, T. Shindo, M. Otsuka, M. Nabeshima,
T. Kurachi, K. Nakagawa, S. Kawakatsu,
S. Akiho, S. Tsurumi, M. Fukasawa,
J. Masuko and T. Aoyama

Researches are being carried on the following subjects:

(1) The work on the hydrogen uptake in the hydride forming metals was extended to iron-titanium alloys. The behavior of hydrogen absorption was observed in gaseous environment, and it was correlated with the composition and the metallurgical structure of the alloys. Diffusion of the absorbed hydrogen in the alloys will be studied by the neutron scattering method. The effect of anodic pre-oxidation upon the rate of electrochemical hydrogen uptake in reactor-grade zirconium was also studied.

(2) Electrochemical study on the corrosion of high nickel alloys in acidic media still continued. Selective dissolution rates of each metallic components were measured under potentiostatically polarized conditions. The potentiostatic polarization characteristics, the ultra low frequency impedances and the ESCA spectra were also measured in order to clarify the corrosion mechanisms.

(3) The reductive dissolution of various kinds of synthesized ferric oxyhydroxides and their calcined products were measured by using the potentiostatic iodometry. The results obtained by this measurement were correlated with that of other observations, such as the X-ray diffraction, the Mössbauer spectroscopy and the BET surface area measurement. We are especially interested in the effect of the primary particle size of ferric oxyhydroxides

upon the above-mentioned properties at present.

(4) Radioactivation analysis with the electron linear accelerator was attempted for the determinations of very small amounts of some elements in various metallic and inorganic substances. For example, several tens ppm of Ga, Mn and Na in aluminum ingot and bauxites were successfully determined. The determination of adsorption isotherm of uranium, which exist several tens ppb in aqueous solution and is adsorbed in the adsorbents made of titanium compounds, is also tested by this method.

(5) The Mössbauer spectra of the iron-titanium alloys and the nickel-chrome steels were measured. The relationships between the Mössbauer spectroscopic features and the properties of the hydrogen adsorption or the anticorrosiveness of these alloys were examined.

(6) Kinetic studies of the oxidation of HTGR fuel particles was pursued in a gaseous oxygen environment with the Gulbransen microbalance. Sigmoid weight gain-time curves were obtained, and the change in the appearance of fuel particle was followed at both of the incubation and the steady periods of the reaction by the SEM method.

Oral Presentations

Application of Etching Method for Measurement of Hydrogen Concentration Profile in Hydride Layer on Zirconium Surface; T. Mizuno, T. Kurachi and T. Morozumi: Joint Meeting of the Hokkaido Section of the Electrochemical Society of Japan and the Corrosion Research Association in Hokkaido; Jan. 1977.

Computer Processing of Mössbauer Spectrum Data; M. Otsuka, H. Ohashi and T. Morozumi: The 1977 Winter Joint Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Anal. Chem. Soc., Feb. 1977.

Effect of Calcination on Structure and Chemical Reactivity of β-Ferric Oxyhydroxide; H. Ohashi, K. Kurokawa, M. Otsuka and T. Morozumi: *ibid.*, Feb. 1977.

Measurement of Hydrogen Concentration Profile of Hydride Layer on Zirconium Surface by the Etching Method; T. Mizuno, T. Kurachi and T. Morozumi: Annual Conference of Japan Society of Corrosion Engineering, May 1977.

Effect of Calcination on Reductive Dissolution and Structure of β-Ferric Oxyhydroxide; H. Ohashi, K. Kurokawa, M. Otsuka and T. Morozumi; *ibid.*, May 1977.

Corrosion of Hastelloy-C in Sulfuric Acid Solution; M. Moriya, T. Aoyama and T. Morozumi: *ibid.*, May 1977.

Rate Law of Dissolution of Uranium Oxides in Nitric Acid Solution; H. Ohashi, S. Kato and T. Morozumi: 1977 Fall Meeting of the Atomic Energy Society of Japan. Oct. 1977.

ELECTROMETALLURGY LABORATORY

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

Students

M. Kawada, H. Okuyama, K. Sugita, K. Kasama,
J. Asano, S. Takeda, M. Kurata,
A. Fukuhara and H. Metoki

Research subjects in this laboratory are as follows.

(1) Laboratory scale tests in the single cells and the bipolar electrode cells for electrowinning of liquid aluminum are being carried out by using alkali and alkaliearth chlorides molten salts containing aluminum chloride in the temperature range from 700° to 800°C. The electrolytic conductivities of these molten salts and the solubilities of aluminum metal to these molten salts are also being measured in this temperature range.

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

(3) To establish protection mechanisms of inhibitor films as well as oxide films formed on metals in corrosive environments, the current major research effort is centered on developing more effective inhibitors for copper and copper base alloys in sea water or in cooling systems. Electrochemical measurements in conjunction with a rotating disk electrode device and immersion tests are being carried out to evaluate protectiveness afforded to the metals by pretreatment with organic inhibitor solutions.

(4) In order to clarify some limitations of electrochemical determination of natural corrosion rate, immersion tests and electrochemical measurements are carried out on iron specimen immersed in acidic solutions of various pH by using rapid polarization and linear polarization techniques.

(5) Immersion tests of various metals also are being undertaken in the low temperature molten salt system such as ammonium bisulfate melts at 200°C.

Oral Presentations

Effect of Recyclic Potential Sweep on Passivation of Stainless Steels; A. Suzuki, T. Ishikawa: 12th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1977.

Tolyltriazole as Corrosion Inhibitor for Copper and Copper Alloys; T. Notoya: *ibid.*, Jan., 1977.

Fundamental Study on Electrowinning of Molten Aluminum from Molten Salt Mixtures of Chlorides —Disintegration of Graphite Cathode and its Prevention—; T. Abe, S. Konda and T. Ishikawa: 3rd Hokkaido Section Meeting of Electrochemical Society of Japan, Jan., 1977.

Determination of the Current through Bipolar Electrode by Split Electrode in Potassium Dichromate Solution; A. Kanazawa, T. Sasaki and T. Ishikawa: *ibid.*, Jan., 1977.

Corrosion Protection of 70/30 Brass with Benzotriazole; T. Notoya: 1977 Winter Meeting of the Hokkaido Region of Chemical Society of Japan, Feb., 1977.

Successive pretreatment for Corrosion Inhibition of Copper; T. Notoya: *ibid.*, Feb., 1977.

Pretreatment Temperature Effect on Protection of Copper and Copper Base Alloys with Benzotriazole; T. Notoya: 44th Annual Meeting of Electrochemical Society of Japan, April, 1977.

Electrowinning of Liquid Aluminum by using Funnel Pile Type Bipolar Electrode Cell (Part 3) Electrochemical Characteristics of Impurities in the Melts; K. Sugita, S. Konda and T. Ishikawa: *ibid.*, April, 1977.

Benzotriazole and Tolyltriazole as Corrosion Inhibitors for Copper and Brasses; T. Notoya and G. W. Poling: Corrosion Research Conerfence, National Association of Corrosion Engineers 77' Annual Conference, San Francisco, March, 1977.

Metallic Corrosion under Heat Transfter Conditions; T. Ishikawa:

Committee of Material for Chemical Process Equipment, Chemical Engineering Society of Japan, April, 1977.

Basic Characteristics of Bipolar Cell on the Reduction of Cr (VI) to Cr (III) ; T. Sasaki, A. Kanazawa and T. Ishikawa : 44th Annual Meeting of Electrochemical Society of Japan, April, 1977.

Effect of Cyclic Potential Sweep on Passivation Characteristics of Stainless Steels ; A. Suzuki and T. Ishikawa : '77 Spring Meeting of the Japan Society of Corosion Engineering, May, 1977.

Benzotriazole and Tolyltriazole Combinations Control Corrosion of Copper Alloys ; T. Notoya : *ibid.*, May, 1977.

Copper Corrosion Protection with Heterocyclic Organic Compounds ; T. Notoya : The Hokkaido Section Meeting of JIM and ISIJ, June, 1977.

Electrowinning of Liquid Aluminum by using Funnel Pile Type Bipolar Electrode Cell (Part 4) Effect of Constitutive Factors of the Cell on Gross Current Efficiency ; K. Sugita, S. Konda and T. Ishikawa : 11th Symposium on Molten Salt Chemistry, Oct., 1977.

Fundamental Studies on ALCOA New Smelting Process (Part 4) Influence of Electrolytic Conditions on Current Efficiency ; H. Ichikawa and T. Ishikawa : *ibid.*, Oct., 1977.

Studies on the Properties of High Temperature Chloride Melts Containing Aluminum Chloride (Part 1) Soluble Characteristics of Aluminum Metal in the Molten Salts ; H. Okuyama and T. Ishikawa : *ibid.*, Oct., 1977.

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

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

Students

T. Iwazaki, M. Kobayashi, K. Kaneko, K. Higashioka,
K. Chiba, K. Takita, I. Nakamura and S. Fukui

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

(1) Researches on thermochemical splitting of hydrogen sulfide.

Conversion of hydrogen sulfide to hydrogen by molten lead, formation of lead sulfate and elemental sulfur by the reaction of SO_2 with lead sulfide and regeneration of metallic lead and SO_2 by the mutual reaction between lead sulfide and lead sulfate are being carried out.

Thermochemical splitting of hydrogen sufide 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 :

$$Fe_3O_4 + 6HCl + H_2S = 3FeCl_2 + 4H_2O + S^\circ$$
$$3FeCl_2 + 4H_2O\,(g) = Fe_3O_4 + 6HCl + H_2$$

(2) Reduction kinetics of metal sulfides by hydrogen.

This study is aimed at finding the mechanism of direct reduction of sulfide ores. Observation of morphologic characteristics of the metals formed from solid sulfides, oxides, chlorides and vapor phase sulfides are being made.

(3) Reduction of metal sulfates with hydrogen.

Measurements of reduction rate, identification of reduction products and reduction mechanism are being investigated on $CuSO_4$, $NiSO_4$, and $CoSO_4$.

(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

Thermal Decomposition of Hydrogen Sulfide with Iron Sulfide; H. Kiuchi, T. Iwazaki, and T. Tanaka: The 1977 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Feb., 1977.

A Closed Loop for the Decomposition of Hydrogen Sulfide with Ferrous Chloride, (I); R. Shibayama, K. Nakajima, and T. Tanaka: *ibid.*, Feb. 1977.

Arsenic Removal from Copper Electrolyte by Solvent Extraction; T. Nagai and M. Kobayashi: *ibid.*, Feb. 1977.

Utilization of Hydrogen Sulfide to Hydrogen Production (III); H. Kiuchi, T. Iwazaki, and T. Tanaka: Annual Meeting of Min. and Metal. Inst. Japan, Apr., 1977.

A Closed Loop for the Decomposition of Hydrogen Sulfide with Ferrous Chloride (II); R. Shibayama and T. Tanaka: *ibid.*, Apr., 1977.

Purification of Copper Electrolyte: M. Kobayashi and T. Nagai: *ibid.*, Apr., 1977.

A Study for the Thermal Decomposition of Hydrogen Sulfide with Metal Sulfides; H. Kiuchi, T. Iwazaki and T. Tanaka: The 36th Annual Meeting of Japan Chem. Soc., Apr., 1977.

Action of Metal Sulfides on the Thermal Decomposition of Hydrogen Sulfide (I); H. Kiuchi, T. Iwazaki and T. Tanaka: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Inst. of Japan, June, 1977.

Reduction of Metal Sulfates with Hydrogen (I) —On the Solid Reduction Products—; R. Shibayama, K. Kaneko and T. Tanaka : *ibid.*, June, 1977.

Recovery of Hydrogen and Sulfur from Hydrogen Sulfide ; H. Kiuchi, T. Iwazaki and T. Tanaka : The Hokkaido Section Meeting of the Min. Metal. Inst. Japan, June, 1977.

On the Reaction between Metal Sulfates and Hydrogen ; R. Shibayama, K. Kaneko and T. Tanaka : *ibid.*, June 1977.

A Process for Treatment of Arsenic Bearing Solutions ; K. Higashioka and T. Nagai : *ibid.*, June, 1977.

Freeze-Melt Process for Recovery of Arsenic Trioxide ; K. Higashioka and T. Nafai : Research Committee for Intermediate Products, Min. Metal. Inst. Japan, June, 1977.

Recovery of Arsenic Trioxide from Copper Electrolyte ; M. Kobayashi and T. Nagai : *ibid.*, July, 1977.

Recovery of Hydrogen from Hydrogen Sulfide by Metal Sulfides ; H. kiuchi, T. Iwazaki and T. Tanaka ; The 1977 Summer Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., July 1977.

Hydrogen and Sulfur Fixing from Sulfide Ores ; T. Tanaka, H. Kiuchi and R. shibayama : Research Committee for Sulfur Fixing in Nonferrous Extractive Metallurgy, Min. Met. Inst. Japan, Aug., 1977.

A Hydrometallurgical Process for Production of Arsenic Trioxide ; T. Nagai, M. Kobayashi and K. Higashioka : Fall Meeting of the Min. Met. Inst. Japan, Oct., 1977.

Action of Metal Sulfides on the Thermal Decomposition of Hydrogen Sulfide, (II) ; H. Kiuchi, T. Iwazaki and T. Tanaka : The Fall Meeting of the Hokkaido Sections of the Japan Inst. of Metals and Iron & Steel Inst. of Japan, Nov., 1977.

Fundamental Studies on the Production of Hydrogen from Sulfides, Report 7 —Utilization of H_2S to Hydrogen Production— ; H. Kiuchi, T. Iwazaki and T. Tanaka : The 4th Symposium on the Hydrogen Energy System, Hydrogen Energy Soc. in Japan, Nov., 1977.

Recoveries of Hydrogen and Sulfur from Hydrogen Sulfide (II) ; H. Kiuchi, T. Iwasaki and T. Tanaka : The Fall Meeting of the Hokkaido Section of the Min. Metal. Inst. Japan, Nov., 1977.

Reduction of Metal Sulfates with Hydrogen (II) —Reduction Mechanism of Cobalt Sulfate— ; R. Shibayama, K. Kaneko and T. Tanaka : *ibid.*, Nov., 1977.

Fundamental Studies on Freeze-Melt Process for Recovery of Arsenic Trioxide ; K. Higashioka and T. Nagai : Research Committee for Intermediate Products, Min. Met. Inst. Japan, Nov. 1977.

PHYSICAL METALLURGY LABORATORY

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

Students

S. Ohnuki, T. Niiyama, T. Hara, T. Edamura,
H. Murakami, T. Matsuhashi, K. Kurokawa,
H. Ohkami, and T. Yanagisawa

In this laboratory, three kinds of electronmicroscope (EM) have been installed: high voltage (650 kV) EM, ordinary type (100 kV) EM and scanning EM. Added to the above three EMs, a newly developed high resolution analytical EM has been introduced. The EM is operated with 200 kV accelerating voltage, equipped with STEM and microanalytical function. High voltage EM has been used to investigate radiation damages induced by accelerated electrons and ions. At present void formation or swelling in iron, vanadium, nickel, copper and their alloys is being extensively studied. Analytical EM could be used to examine precipitation or segregation accompanied by radiation. An ultra-high temperature tensile testing apparatus with electron beam furnace has been developed to study the mechanical properties of molybdenum and its alloys at high temperatures. Fractographic analysis using SEM is applied to investigate hydrogen blistering and cracking of pure iron and also to stress corrosion cracking of titanium in organic solvents containing iodine. Pitting corrosion of stainless steels and other high nickel alloys is analyzed based on the stochastic theory. Pit generation process is found to be consisted of several parallel processes, the rate of which depends on the potential applied.

Oral Presentations

Effect of Surface Treatments on Corrosion Behavior of Stainless Steels; T. Shibata: 8th Symposium on Corrosion and Prevention, Jan. 1977.

Surface Area Dependence of Pitting Potential; T. Shibata and T. Takeyama: 12th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 1977.

Precipitation Phenomena in Vanadium-Low Oxygen Alloys; T. Edamura, H. Takahashi and T. Takeyama; The Hokkaido Section Meeting of Japan Sociaty for Electronmicroscopy, Feb. 1977.

Solvent Effects on the Stress Corrosion Cracking of Titanium; T. Shibata, T. Takeyama and K. Kasama; The Spring Meeting of the Japan Institute of Metals, April, 1977.

Void Formation of Nickel by Electron Irradiation and Pre-strain Effect; T. Sawada, H. Takahashi and T. Takeyama: *ibid.*, April, 1977.

Structural Change in Precipitation Process of Vanadium-Carbon Alloys; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid,* April, 1977.

Void Formation of Iron by 200 keV C^+ Ion Irradiation; H. Takahashi, T. Takeyama, S. Nakahigashi and T. Terasawa: *ibid,* April, 1977.

Surface Area Dependence of Pitting Potential; T. Shibata and T. Takeyama: Annual Conference of the Japan Society of Corrosion Engineering, May, 1977.

Precipitation during Aging in Vanadium-Low Oxygen Alloys; T. Takahashi, T. Edamura and T. Takeyama: The Seminar on Refractory Metals and Materials sponsored by the Japan Institute of Metals, May, 1977.

Effect of Oxygen on the Stress Corrosion Cracking of Titanium; T. Shibata, T. Takeyama and Y. Tetsuka: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, June. 1977.

Irradiation Effect of Fe-Mn-C Alloys; S. Ohnuki, H. Takahashi, T. Takeyama and H. Kayano: The Fall Meeting of the Japan Institute of Metals, Oct. 1977.

Structural Change during Aging of Vanadium-Oxygen Alloys: T.

Edamura, H. Takahashi and T. Takeyama: *ibid,* Oct. 1977.

Pit Generation Process of Inconel 600; T. Shibata and T. Takeyama: *ibid,* Oct. 1977.

Straining Electrode of Type 304 Stainless Steel in High Temperature 20% NaCl Solutions; T. Shibata and T. Takeyama: The Fall Meeting of the Japan Society for Iron and Steel Institute, Oct. 1977.

Hydrogen Charge in Iron-Nickel Alloys; K. Matsuhashi, H. Takahashi and T. Takeyama: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, Nov. 1977.

Effect of Deformation Temperature on the Structure of High Manganese Steels; T. Hasegawa, H. Takahashi and T. Takeyama: *ibid,* Nov. 1977.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

Y. Sugawara, K. Miyagi, Y. Izumi, A. Uemura,
H. Shinoda, Y. Fujita, T. Maejima
and T. Yamada

In this laboratory, researches are being conducted mainly on the strength and the high-temperature properties of cast iron. Besides, the study on the bending creep of steel and the failure analysis of machine members, etc., are being conducted.

Research subjects are listed as follows:

(1) The bending strength of cast iron disks with a variety of thickness, diameter and the grade of strength were tested by one-point loading. Experimental results were formulated by a similar non-elastic analysis made in the previous works.

(2) Propagation of bending fracture in cast iron disk under stepwise loading was observed by means of a optical projector. The micro-fracture initiated at the load level of 70 per cent of the maximum. The final rupture occurred after the load reduced down to 60 per cent of the maximum.

(3) In order to investigate the growth characteristics of cast iron, the dilatometric curves were examined in gas mixture of argon and oxygen with specimens of as cast and grown iron. The dilatometric curve of the grown iron remarkably depended on the atmosphere; iron contracted in vacuum, but expanded in dilute-oxygen and argon gas mixture.

(4) Using the quantitative television microscope (LUZEX), a particle image analysis was applied to evaluate the properties of S. G. iron.

The tensile strength of the iron was proportional to the size and the number of graphite nodules for the same carbon content and microstructure of matrix.

(5) As observed previously by an optical microscope, the graphite increases the size, the number and the farctional area of grown iron. In order to examine these changes quantitatively, a particle image analysis with Q.T.M. (LUZEX) was applied to the grown S. G. iron. Fractional area of graphite phase in 10% growth in length was 2.0 times as large as the fractional area in as cast iron, and after the growth, a great number of samll particle of graphite with diameter less than 10 μm were observed.

Oral Presentations

On the Bending Strength of Cast Iron Circular Plate; T. Noguchi and K. Nagaoka: The 91th Grand Lecture Meeting of the Japan Foundrymen's Society, May 1977.

Effect of Dilute Oxygen on the Dilatometric Curves of Cast Iron; M. Sōma and K. Nagaoka: The 91th Grand Lecture Meeting of Japan Foundrymen's Society, May 1977.

Recent Development in Fractography; K. Nagaoka: The Lecture Meeting on Labor Safety (Hokkaido), June 1977.

On the Bending Fracture of Cast Iron Disk; T. Noguch and K. Nagaoka: The Hokkaido Section of Lecture Meeting of The Japan Foundrymen's Society, June 1977.

Quantitative Analysis of Graphite Phase in S. G. Iron; M. Sōma, K. Nagaoka, T. Noguchi and N. Shiramine: The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1977.

Stress-Stain Curves of Cast Iron at Subnormal Temperature; T. Noguchi and K. Nagaoka: The 92nd Grand Lecture Meeting of Japan Foundrymen's Society, Oct. 1977.

Fracture of Steel Structures; K. Nagaoka: The Hokkaido Section Lecture Meeting by Societies of Weld Engineering and Civil Engineering, Oct. 1977.

Failures of Machine Parts and Factor-Analysis; K. Nagaoka: The

Course on Failures and Non-destructive Inspection of Machine Parts by The Hokkaido Section of The Japan Society of Mechanical Engineering, Nov. 1977.

Effect of In Situ Heating of ε-Carbide Irradiated by Means of H.V.E.M.

T. Takeyama and H. Takahashi

Proc. US-JAPAN HVEM Seminar, New Applications
and Extentions of the Unique Advantages of
HVEM for Physical and Materials
Research, p. 111 (1977)

Iron-carbon alloy containing 0.025 wt% carbon was solution treated at 730°C for 1 hr and then quenched into iced water. The specimen was aged for 25 hrs at 105°C to obtain the precipitations of ε-carbides. After these treatments, foil specimens for observation of transmission electron microscopy were prepared and were electron-irradiated at room temperature to fluence of $10^{20} \sim 10^{21}$ e/cm^2 in HVEM. When the unirradiated foil was aged at 200°C, ε-carbides formed in the foil were dissociated and dissolved into matrix and cementites were simultaneously formed. On the other hand, ε-carbides in the electron-irradiated area still remained at 200°C without resolution of the precipitates. However, the ε-carbides irradiated began to dissolve at 250°C and a number of small black dots appeared along the sites where ε-carbides were formed. From these experiments, it was concluded that the small dots might be nucleated at the complexes of irradiation-produced-defects and carbons which had been composed of ε-carbides. Furtheremore, it was clarified from the character determination of loop that the dots were the loops of interstitial type. (English).

On the Growth of Forged Spheroidal Graphite Cast Iron

M. Sōma and K. Nagaoka

IMONO, **49**, No. 8, 495 (1977)

Growth characteristics of forged S. G. iron with flattened graphite nodules was examined by cyclic heating to 950°C in air. Forging was applied to as cast and pre-grown irons with forging ratio of 25% and 50%. The growth of S. G. iron increased by the forging and the effect was shown markedly in the pre-grown iron.

The growth increased by about 20% with the forging ratio of 25%, and by 10% with the ratio of 50%. After cyclic heatings a preferential precipitation of graphite was observed at the tip of flattened graphite nodules. Without any change of microstructure of matrix, the forged iron showed remarkable increase of specific gravity and hardness.

The iron grown 10% previously in air was very low growth characteristics, but the forging with reduction of 25% the growth increased more than 2.0 times. The recovery of growth characteristics by forging in the pre-grown iron may be explained by the growth mechanism of irreversible migration of graphite. (Japanese)

Observation of the Growth of Spheroidal Graphite Cast Iron by Scanning Electron Microscope

K. Nagaoka and M. Sōma

IMONO, **49**, No. 12, 742 (1977)

In order to investigate the growth characteristics of S. G. iron, the fracture surface of the iron which grew up in air to 10% in length was observed by SEM and XMA equipped. From SEM-XMA fractography and microanalysis of compositions, evidences for the growth mechanism of irreversible migration of graphite were given as micro-voids around graphite nodules and re-distribution of graphite in the matrix.

No effect of oxidation was observed by XMA analysis of O and Si in the central area of the specimen grown up to 10% in length. This result is very important in discussing the growth mechanism in relation to the oxidation theory. (Japanese)

A Study on Transverse Deflection of Cast Iron Beams

T. Noguchi and K. Nagaoka

IMONO, **49**, No. 2, 63 (1977)

The rupture deflection of beams in transverse test are used to evaluate indirectly the ductility of cast iron. In this paper the rupture deflection of beam was related successfully to the tensile rupture elongation by an inelastic analysis for the stress-strain properties of cast iron. Using an electronic computer the load-deflection curve of a cast iron beam with an arbitrary cross section was analyzed well by a numerical method. According to the experimental procedure, cast iron beam did not rupture at the theoretical deflection value under the maximum stress condition.

A "factor of bending strain" (bending rupture strain/tensile rupture strain) was effective to relate the rupture deflection to the tensile rupture strain. For average value of the factor of bending strain, the deflection of 6–10 mm in the transverse test was equivalent to the tensile strain of 0.4–1.2%. The factor of bending strain depends not only on the strength of cast iron but also on the dimensions of beam and surface conditions. The rupture deflection of irons with cast surface was reduced remarkably. (Japanese)

High Temperature Oxidation of Calorized Ta Sheets

K. Nishida and M. Hachinohe

The Journal of the Metal Finishing Society
of Japan, 28, No. 11, 570 (1976)

The oxidation behavior of Ta sheets, calorized at 1000°C for 16 hr, has been examined in flowing air (1 L/min) over the temperature range from 900 to 1300°C. At 1100°C, the weight gain was only 0.45 mg/cm^2 with no further change in weight and was found to be a minimum comparing with those at other testing temperatures. This seems to be attributable to the fact that a double oxide ($TaAlO_4$) is formed sufficiently to prevent further oxidation at this temperature. At 900°C, the alloy layer was mostly oxidized into oxides (Ta_2O_5 and Al_2O_3), whereas, at 1000°C, the inner part of the alloy layer remained unoxidized, but the alloy changed into lower aluminides (TaAl and Ta_2Al), and $TaAlO_4$ as well as Ta_2O_5 were found in the scale. At high temperature such as 1300°C, all of the alloy layer changed into Ta_2Al compound. Only a small part of aluminum in the $TaAl_3$ alloy penetrated into the Ta substrate during oxidation at lower temperatures, while almost all aluminum was oxidized into Al_2O_3 oxide. At higher temperatures than 1100°C aluminum penetrated more easily, forming voids in the alloy layer, but some of aluminum in the alloy changed, at first into Al_2O_3 oxide in the scale. This oxide still prevents the oxidation, but the accumulation of such voids in the alloy layer will result in a sudden breakaway. (Japanese)

Chemical Diffusion in Fe-Sb Alloys

K. Nishida, H. Mitsuhashi and T. Yamamoto

Journal of the Japan Institute of Metals,
41, No. 11, 1101 (1977)

Iron test pieces were diffusion-annealed in an evacuated silica capsule containing the powdered (100∼200 mesh) 50 wt% Sb-Fe alloy consisting of α and ε phases as an Sb vapor source for 9∼400 hr at 700∼950°C. The test pieces were then analysed with an EPMA and the penetration curves of them were obtained.

Each penetration curve was analysed by means of the Matano-Boltzamann method to obtain the chemical diffusion coefficients ($\tilde{D}$). From these values the activation energies for diffusion ($\tilde{Q}$) were calculated.

Surface concentration of the test pieces (α_{max}) at each annealing temperature coincided approximately with the solubility observed in the phase diagram of an Fe-Sb system at lower temperatures, while a significant deviation was found in solubility at higher temperatures. Fine alumina makers placed on the test pieces prior to diffusion were found always on the surfaces after annealing so that it was considered that Sb atoms diffused predominantly in the α-phase of this system. Each penetration curve was similar to an error function curve and $\tilde{D}$ at each temperature showed a relatively small dependence upon Sb concentration. There was a gap in the Arrhenius plot owing to magnetic transformation. The activation energies for diffusion ($\tilde{Q}$) obtained from the data at higher temperatures varied from 59.5 kcal/mol for 1 at% Sb to 52.5 kcal/mol for 4 at% Sb and that for impurity diffusion of Sb in iron (Q^{*}_{sb}) was evaluated to be about 63 kcal/mol. (Japanese)

The Effect of Fe (III)-oxyhydroxides on the Oxygenation of Fe^{2+} Ions

H. Tamura, K. Takahashi and M. Nagayama

Bulletin of the Faculty of Engineering, Hokkaido
University, No. **85**, 93 (1977)

The oxygenation of Fe^{2+} ions is accelerated by the Fe (III)-oxyhydroxides (amor-Fe $(OH)_3$ and α-, β-, γ-FeOOH) in neutral solutions. For constant pH and $[O_2]$, the reaction rate is expressed by

$$\frac{-d\,[\mathrm{Fe}^{2+}]}{dt} = \{k+k'\,[\mathrm{Fe\,(III)}]\}\,[\mathrm{Fe}^{2+}],$$

where Fe (III) represents the oxyhydroxides ; k is the rate constant for the "homogeneous reaction" occurring in the solution and k' is the rate constant for the "heterogeneous reaction" catalysed by Fe (III). The value of k' decreases in the order of amor-$Fe(OH)_3$ $>\alpha$-FeOOH$>\gamma$-FeOOH$>\beta$-FeOOH. The catalytic effect is due to the fact that Fe^{2+} ions adsorbed on Fe (III) are more reactive to O_2 than the free Fe^{2+} ions in the solution. For a given pH and $[O_2]$, k' is equal to the product of the equilibrium constant for the adsorption (K) and the specific rate constant for the oxygenation of the adsorbed $Fe^{2+}(k_s)$. The values for K and k_s were determined as functions of pH and $[O_2]$ for each Fe (III) species. (Japanese)

Effect of Calcination on Reductive Dissolution and Structure of γ-Ferric Oxyhydroxide

H. Ohashi, H. Goto, K. Hirohara and T. Morozumi

J. Electrochem. Soc. Japan (Denki Kagaku),
45, 569 (1977).

The rate of reductive dissolution of the calcined products, obtained from γ-ferric oxyhydroxide, was measured in a potentiostatically controlled sodium iodide-triiodide solution. The rate increased with an increase in calcination temperature below 350°C and decreased rapidly above 450°C. The TG and the DTA measurements indicated an increase in the reactivity with calcination temperature, which could be ascribed to the dehydration of the oxyhydroxide at the lower temperatures. Two distinct phase changes, the appearance of γ-ferric oxide at 350°C and the transformation from this phase to α-ferric oxide above 450°C, were observed by the X-ray diffraction. The latter phase change is likely to contribute mainly to the reduction of the reactivity. In the case of calcination temperature nearby 350°C, the broadening of the X-ray diffraction lines and the disappearance of the Mössbauer absorption peaks were observed. The iron atoms in these products seem to take the loosely bound state in which the atoms can be easily recoiled on irradiation with the low energy electromagnetic particles. These unstable nature of iron atom-bonding may contribute to the high reactivity of the products obtained at intermediate temperatures. (English)

Oxidation or Reduction of Ferrous Sulfate and Other Solid Inorganic Substances Induced by γ-Irradiation

T. Morozumi, H. Ohashi, K. Nakazawa
and T. Funakoshi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. **84**, 91 (1977)

Pulverized solid specimens of ferrous sulfate and another twenty kinds of inorganic substances were irradiated with cobalt-60 γ-ray, and the variations in amounts of oxidative or reductive reactions to the potentiostatically controlled iodide-triiodide redox system were measured. Although most of these substances were more or less oxidized or reduced following irradiation, the irradiation effect was most remarkable on ferrous sulfate. Ferrous sulfate was oxidized by the irradiation and it was shown that the amount of oxidation was almost linearly proportional to the exposure within some limitation. The iradiation effect was quite stable when accompanied by practically no fading for a long cooling period. In this sense, ferrous sulfate seems to be the most feasible material for the solid chemical dosimetry. Since the amount of oxidation of the irradiated ferrous sulfate was strongly dependent upon the amount of hydration, the first step of this reaction may be the decomposition of the water of crystallization. The maximum value of G(Fe^{3+}) was about 6 and it was much smaller than that in the aqueous solution containing salt. (Japanese)

Topographies of Copper-benzotriazolate Film and Underlying Copper Oxide

T. Notoya and G. W. Poling

J. Electrochem. Soc. Japan (DENKI KAGAKU),
45, No. 1, 49 (1977)

Surface topographies of thick (2000 Å) copper-benzotriazolate (CuBTA) films and underlying copper oxides have been demonstrated in scanning electron micrographs. CuBTA films were formed on a coarse grained polycrystalline copper in acidic chloride solution in the presence of benzotriazole. The valence state of copper in thick CuBTA films was confirmed to be cuprous rather than cupric by ESCA analysis. Relations to crystallographic orientations of substrate copper crystals and structure of Cu_2O interlayers have also been described. Although the structure of thick CuBTA films formed on top of the oxide was influenced by the oxide thickness, they appeared to be less dependent on the crystallographic orientation of the substrate copper crystal. (Japanese)

Passive Films on Iron in Neutral Boric-Borate and Phosphate and Phosphate Solutions

Rokurou Nishimura and Norio Sato

Corrosion Engineering (Boshoku Gijutsu),
26, No. 6, 305 (1977)

The passive films on iron in neutral boric-borate and phosphate solutions at +0.845V (S. H. E.) for 1 hour have been investigated by using electrochemical, ellipsometric and Auger spectroscopic techniques.

From analyses of iron dissolution and δP-δA curves during galvanostatic reduction of the film, it was found that the passive films formed in these solutions consisted of a deposit layer and a barrier layer, and that the composition of the two layers was different in different anion solutions. In boric-borate solution, the deposite layer which grows to 26A was in the oxidation state of iron (III) with the optical constant of 2.20-0.10 i and the barrier layer growing to 22A was in the same oxidation state of iron (III) with the optical constant of 2.50-0.30 i. In phosphate solution, the deposit layer with the optical constant of 2.20-0.14 i showed the mean oxidation valency of iron $Z_{Fe}=2.94$ at the thickness 32A, whereas the barrier layer was in the mean oxidation state of $Z_{Fe}=2.33$ and had the optical constant of 2.50-0.35 i at 18A.

It was also found that there were a iron-depletion or oxygen-excess layer at the deposit/barrier interface and a OH radical or O^- adsorption layer at the deposit/solution interface of the passive film formed in boric-borate solution. No specific adsorption or depletion, however, was found in the passive film formed in phosphate solution.

The Auger spectroscopic measurements revealed that both the deposit layer and the barrier layer formed in phosphate solution contained phosphorus ions, whereas the passive film formed in boric-borate solution contained boron ions only in the deposit layer.

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

Ion Migration in Anodic Barrier Oxide Films on Iron in Acidic Phosphate Solutions

Norio Sate and Tetsuji Noda

Electrochimica Acta, **22**, No. 8, 839 (1977)

A kinetic study was carried out of the ionic current in the anodic barrier oxide layer on iron at the steady state in the passive potential region in acidic phosphate solutions. It is found that the ionic current follows the classical high field ion conduction equation in which the current is expressed as an exponential function of the electric field in the barrier layer. From the kinetic constants appearing in this equation and their temperature dependence, the diffusion coefficient and the activation energy for diffusion of moving ions in the layer were estimated and compared with those of high temperature diffusion in iron oxides. It is suggested that the ionic current is carried by oxygen ions rather than by iron ions in the barrier oxide film. (English)

Auger Analysis of the Anodic Oxide Film on Iron in Neutral Solution

M. Seo, N. Sato, J. B. Lumsden and R. S. Staehle

Corrosion Science, **17**, No. 3, 209 (1977)

The composition depth-profile of anodic oxide films on iron at various potentials in a boric acid-sodium borate solution of pH 8.4 was measured by the sequential use of Auger electron spectroscopy (AES) and sputter-etching. It was found that the anodic oxide film consisted mainly of oxygen and iron with minor impurities such as boron, sulphur and carbon. The composition ratio of boron or sulphur to oxygen exhibited a maximum value at a certain depth in the outer layer of the film and the maximum value of (B/O) increased with increasing potential up to 500 mV (SCE). The film formation mechanism is discussed from the observed dependence of boron content in the film. (English)

Corrosion and Passivation of Iron-Chromium Alloys

M. I. Ismail and N. Sato

Bulletin of the Faculty of Engineering, Hokkaido
University, **83,** 147 (1977)

The corrosion and passivation of Fe–Cr alloys, heat-treated with different cycles, then subjected to different environmental conditions, were studied using metallographic, electrochemical and chemical techniques. On exposure of the thermally formed oxide films to air, for 8 months, the films formed on rapidly cooled specimens (Water Quenched, WQ) proved to be more protective than those formed on slowly cooled specimens (Furnace Cooled, FC). Potentiostatic polarization in sulfuric acid indicated that the rate of corrosion (current density) decreases with increases of Cr content, with a minimum value for the alloy 10 Cr. The grains varied in their susceptibility to attack. Some specimens were characterized by corrosion-resistant bands on the surface. The rate of passivation (current decay ratio) increased with increase of the temperature of heat-treatment and with an increase of Cr content for air cooled specimens (Air Cooled, AC). Thermal cycling lead to a decrease in the anodic current decay ratios. WQ specimens had lower current densities than FC or AC ones.

Spectrophometric analysis of the electrolyte after electrolysis indicated that Cr dissolved from FC specimens with higher rates than from WQ for the 5 Cr alloy, but for 20 Cr alloy, the reverse was true. The dissolved Cr increased with increase of Cr content for WQ while for AC specimens, no influence was seen. The dissolved metal ratio (Fe/Cr) had a maximum value at the alloy 10 Cr for WQ specimens, but for FC specimens this ratio decreased with Cr content of the alloy. However, if the heat-treatment cycle was repeated in FC type then the Fe/Cr ratio increased with increase of Cr content. (English)

Effect of Cathodic Pretreatment on the Passivation of Iron in Neutral Solution

A. Rauscher, H. Konno and M. Nagayama

Electrochim. Acta, **22,** 823 (1977)

Pure iron specimens anodically oxidized at +600 mV (vs. sce) for one minute were partially reduced with a cathodic current of 10 μA/cm^2 and then reoxidized at the same potential for one hour. The experiment was performed in a boric acid-borate buffer solution at pH=8.43 at room temperature. Variation in the thickness of the oxide film during the experiment is discussed for an inner Fe_3O_4 and outer γ-Fe_2O_3 layers, with emphasis on the effect of cathodic treatment. In the discussion, the amounts of charges for anodic and cathodic processes and the amount of dissolved Fe^{2+} ions during cathodic reduction are utilized. (English)

The Effect of Current Density and Temperature on the Anodic Oxidation of Aluminum in Sulfuric Acid and Oxalic Acid Solutions

M. Koda, H. Takahashi and M. Nagayama

J. Metal Finishing Soc., Japan, **28,** No. 11, 584 (1977)

99.99% Al specimens were anodized in 10% H_2SO_4 and 2% $H_2C_2O_4 \cdot 2H_2O$ solutions at 20, 30 and 40°C by applying a constant current, i_a, in the range 0.5–100 mA/cm^2. The anode potential, E_a, and the dissolution current of oxide, i_d, were measured during anodization. The porosity, α, and the thickness, h, of the formed oxide were measured as functions of current and temperature. Plots of E_a against log i_a were always S-shaped curves which tend to shift to lower potential region with increasing temperature. It was found for fixed anodic charge that i_d/i_a (dissolution ratio) and α decrease with increasing current and decreasing temperature. The decreases in i_d/i_a and α are always accompanied by an increase in the total film-thickness, h. Transport numbers for Al^{3+} and O^{2-} ions in the barrier layer, $T_{Al}{}^{3+}$ and $T_O{}^{2-}$, were calculated on the assumptions that Al^{3+} ions move into the solution without forming oxide at the barrier layer/solution interface and that part of the oxide produced at the barrier layer/metal interface, due to O^{2-} migration, dissolves into the solution to form a porous layer. The figure obtained for $T_{Al}{}^{3+}$ was in the range 0.25–0.40 and it was found to increase with decreasing current and rising temperature. (Japanese)

Formation and Dissolution of Porous Anodic Oxide Films on Al in a H_2SO_4-$H_2C_2O_4$ Solution

H. Takahashi, K. Yamada and M. Nagayama

J. Metal Finishing Soc., Japan, **28,** No. 5, 286 (1977)

Al Specimens were anodically oxidized in solutions of (1) 10% H_2SO_4, (2) 2% $H_2C_2O_4 \cdot 2H_2O$ and (3) 10% H_2SO_4 − 2% $H_2C_2O_4 \cdot 2H_2O$ by applying a constant c.d. of 9.4 mA/cm^2 at 27°C, and the time-variation in the amount of dissolved Al ions, W_d, was measured by the oxinate extraction method. The weight and geometrical structure of the oxide were also examined at time intervals during anodization. The applied anode potentials were 12.0, 45.0 and 13.5 V (vs SCE) for solutions (1), (2) and (3), respectively. The geometrical structure (cell size, pore-wall thickness, pore-radius etc.) of the porous oxide formed in solution (3) was much more like that formed in solution (1) than to that formed in solution (2). The densities of the oxides formed in solutions (1), (2) and (3) were estimated to be 2.7, 2.8 and 3.0, respectively. The dissolution rate of oxide at the pore-wall, v_s, and that at the pore base v_b, were calculated from W_d in the manner reported previously. The result shows that v_s decreases from solution (1) through (2) to (3), whereas v_b decreases in the order, (2), (3), (1). Thus, it is advantageous to add a small amount of oxalic acid to sulfuric acid anodizing solution. The reason of this is summarized as follows: a) Current efficiency for the formation of oxide considerably increases. Powdering of the oxide could be prevented because of a small value of v_s. b) Electric power does not increase very much, and it is much smaller than that consumed in the anodization in oxalic acid solutions. c) Density of oxide increases remarkably and it is even higher than that obtained by anodization in oxalic acid solutions. (Japanese)

Auto-Oscillation of the Corrosion Potential of Zirconium in Ammonium Fluoride Solutions

M. Moriya, T. Sawaki, M. Mizuno and T. Morozumi

J. Electrochem. Soc. Japan (Denki Kagaku),
45, 636 (1977)

A time variation was observed in the corrosion potential of electropolished zirconium in both pH-controlled and uncontrolled solutions of ammonium fluoride. In the pH-uncontrolled solutions, auto-oscillation of the potential occurred after an induction period which varied from several hours to several dozen hours, according to the concentration of ammonium fluoride, and the period minimized at a concentration of about 0.2 M. In the pH-controlled solutions, the corrosion potential varied remarkably with pH, and sudden changes were observed at certain pH boundaries which were function of the concentration. When pH was fixed at such a boundary the potential oscillation could occur without prolonged induction. On the basis of thermodynamic considerations, the pH boundary can related to the equilibrium between the zirconium-fluoride ion complex and zirconium dioxide. The cyclic changes in both the surface state of zirconium and the pH of the solution near the surface may possibly be linked and they may stand in a causal relation to the periodic oscillation of the corrosion potential. (Japanese)

Periodic Changes in the Impedance of Zirconium in Ammonium Fluoride Solutions Accompanying the Oscillation of Corrosion Potential

M. Moriya, T. Hirota and T. Morozumi

J. Electrochem. Soc. Japan (Denki Kagaku),
45, 724 (1977)

Periodic changes in impedance accompanying the auto-oscillation of the corrosion potential were observed in pH-uncontrolled solutions of ammonium fluoride. A sinusoidal voltage with constant amplitude was applied between the specimen and the auxiliary platinum gauze electrode, and alternating current with the same frequency was picked up through an active-filtered amplifier and recorded. Both the real and the imaginary parts of the impedance were obtained from the amplitude ratio of voltage versus current and the deviation of phase angle. In the induction period before the potential oscillation began, the impedance was relatively small and was related to the active state of zirconium. However, after the oscillation began, the impedance increased and oscillated with the same period as that of corrosion potential. The impedance in the latter state may be expressed with a parallel combination of frequency-independent resistance R_f and the frequency-independent capacitance C_f. Since "frequency-independence resistance" ordinarily means the resistance due to the electrolytic solution or the charge transfer stage, the surface state, which is correlated to the above-mentioned equivalent circuit model, must be a composite of the activated and the passivated portions. It seems possible that the fluctuations in the relative ratio of the active versus the passive areas and also in the thickness of the surface oxide layer both influenced the mode of impedance oscillation. (Japanese)

The Effect of Molybdate Anion on the Ion-Selectivity of Hydrous Ferric Oxide Films in Chloride Solutions

Masao Sakashita and Norio Sato

Corrosion Science, **17,** No. 6, 473 (1977)

The ion-selective property of hydrous ferric oxide precipitate films has been investigated by measuring membrane potentials which arise across precipitate membrances of hydrous ferric oxide with and without adsorbed MoO_4^{2-} ions and of ferric molybdate in solutions of NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $AlCl_3$, and $FeCl_3$. The hydrous ferric oxide membrane was only permeable to Cl^- ions in chloride solutions, whereas the membrane with adsorbed MoO_4^{2-} ions was permeable to cations in NaCl and KCl solutions, and to both Cl^- and cations in the presence of multivalent cations. The ferric molybdate membrane was permeable to Cl^- and cations in NaCl and KCl solutions, and only to Cl^- ions in the presence of multivalent cations. It is suggested that in chloride solutions, the corrosion of iron covered with a precipitate film of hydrous ferric oxide is accelerated by enrichment of Cl^- ions under the film, which may decrease the local pH and introduce a positive diffusion potential in the film. The adsorption of MoO_4^{2-} ions on the oxide changes the ion-selectivity of the precipitate film from the anion-selective to the cation-selective in solutions of NaCl and KCl. This cation-selectivity of the film may inhibit the corrosion of iron, because of H^+ ions diffusing out of the film. The inhibitive effect of MoO_4^{2-} ions would be reduced in the presence of multivalent cations. (English)

Ion Selectivity of Hydrous Iron (III) Oxide Precipitate Membranes

Masao Sakashita, Yoshinori Yomura and Norio Sato

J. Electrochem. Soc. Japan (Denki Kagaku),
45, No. 3, 165 (1977)

The ion-selectivity of hydrous iron (III) oxide precipitate membranes with and without adsorbed MoO_4^{2-} ions has been studied by means of membrane potential measurements. The membrane without adsorbed MoO_4^{2-} ions exhibited an anion-selective property in mono-mono-and multi-monovalent electrolyte solutions, the order of the selectivity for anions being $ClO_4^- < I^- \lesssim No_3^- < Br^- < Cl^-$. In mono-divalent electrolyte solutions such as Na_2SO_4 and Na_2CrO_4, however, this membrane showed the selectivity for cations. The membrane with adsorbed MoO_4^{2-} ions showed a high selectivity for cations in mono-mono-and mono-multivalent electrolyte solutions, but was permeable to both anions and cations in multi-monovalent electrolyte solutions. The implications of this study in the corrosion of iron and steels covered with precipitate film of hydrous iron (III) oxide are discussed. (Japanese)

Effects of pH on Ion-Selectivity of Hydrous Iron (III) Oxide Precipitate Membrane

Masao Sakashita and Norio Sato

J. Electrochem. Soc. Japan (Denki Kagaku),
45, N0. 4, 238 (1977)

The effect of pH on the ion-selectivity of a hydrous iron (III) oxide precipitate membrane has been studied by measurement of membrane potential and surface charge. In chloride solutions of monovalent cations, it was estimated from the pH dependence of membrane potential that the membrane is anion-selective below pH 10.3 and becomes cation-selective in more basic solutions. The pH at which ion-selectivity (and hence the sign of fixed charge on the membrane) changed is not consistent with the point of zero charge (pH_{PZC}), which was found by means of acid-base titration of the membrane to be 8.6. From comparison between experimental and theoretical potentials based on the fixed charge theory of membranes, it was found that the concentration of positive charges fixed on the hydrous iron (III) oxide precipitate membrane is independent of pH in neutral and acid solutions, although surface charge density depends on pH. Furthermore, the membrane is cation-selective in neutral solution containing SO_4^{2-} and CrO_4^{2-} ions, and anion-selective in basic solutions containing Ca^{2+} and Ba^{2+} ions. In both cases, the divalent ions binding strongly with the surface charge actually act as a fixed charge, with a sign opposite to that of the surface charge. (Japanese)

Bipolar Fixed Charge-Induced Passivity

Masao Sakashita and Norio Sato

J. Electrochem. Soc. Japan (Denki Kagaku),
45, No. 12, 744 (1977)

Polarization measurement of hydrated metal oxide membranes was carried out to study the influence of corrosion products covering metal surfaces on the anodic dissolution. Adsorption of divalent anions such as WO_4^{2-} ions on one side interrupted the anodic ion current passing through the hydrated metal oxide membranes. This suggests that the hydrated metal oxide films with positive charge on metal side and with negative charge on solution side (the so called-bipolar membrane) would induce passivity. (Japanese)

Statistical Variation of Pitting Potential for Stainless Steels

Toshio Shibata and Taro Takeyama

Corrosion Engineering (Boshoku Gijutsu),
26, 25 (1977)

Repeated measurement of pitting potentials has been accomplished for 304 and 316 stainless steels in 3.5% NaCl solution deaerated with nitrogen gas at 35°C, using a potentiokinetic method (20 mV/min). Chemical etching using 30% H_2SO_4 for 10 min at 35°C or mechanical polishing with 2/0 emery paper is used for surface preparation. It is clarified that measured values are discribed as a normal distribution, which is easily demonstrated by plotting measured values arranged in ascending order and corresponding probability in a normal probability paper. Although a well controlled condition is used, fairly large standard deviation, or coefficient of variation, is found, the order of which is comparable to that of fracture strength of solid material. Application of "the weakest link model" which is originally developed in fracture phenomena to pitting corrosion is suggested. (Japanese)

Stochastic Theory of Pitting Corrosion

T. Shibata and T. Takeyama

Corrosion Vol. 33, 243 (1977)

Statistical variation of pitting potential and induction time for pit generation has been studied based on a stochastic theory which had been developed for the fracture of solid materials caused by applied stress. In order to obtain a large number of data, a multichannel pitting corrosion testing apparatus was developed, which can measure the pitting potential, or the induction time for 12 specimens in 1 experiment using 1 potentiostat. Analysis of experiment data for Type 304 stainless steel in 3.5% NaCl solution clarifies that the pitting process at a constant potential consists of 3 successive processes, each of which has a different pit generation rate depending on the potential and time. Only the first process is detected by the pitting potential determined by the potential sweep method. Experiment proves the prediction given by the theory that the pitting potential increases with the square root of the potential sweep velocity. Linear dependence of the pit generation rate on the potential suggests that the pitting process is controlled not by an electrochemical reaction, but by an electromechanical breakdown of the passive film. (English)

Changes in Surface Composition of Clean Copper-Nickel Alloys with Ion Bombardment and Annealing

Kuniaki Watanabe, Masao Hashiba, Yasuo Fukuda
and Toshiro Yamasahina

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 83, 139 (1977)

Changes in the surface composition of clean Cu-Ni alloys with ion bombardment and annealing were investigated by Auger spectroscopy. The surface compositions were compared systematically for 8 Cu-Ni alloys by Auger spectra in the lower energies around 100 eV or thereabouts with the higher energies at 700∼1000 eV.

It was found that the surface layers were considerably enriched with Cu atoms by annealing, but the Auger peak of Ni in a lower energy region did not disappear by high temperature annealing even at 600°C for all Cu-Ni alloys.

The configuration of component distribution in several atomic layers at the surface of Cu-Ni alloys was proposed by utilizing the difference in escape length of the Auger electrons from different transitions. (English)

A Quantitative Analysis of Clean Surfaces of Cu-Ni Alloys by Auger Electron Spectroscopy

— Surface Segregation and In-depth Profile —

Kuniaki Watanabe, Masao Hashiba
and Toshiro Yamashina

The Asahi Glass Foundation for the Contribution
to Industrial Technology-Annual Report,
29, 391 (1976)

The surface compositions of clean surface of Cu-Ni alloys with ten different bulk compositions in the whole range were measured by means of the Auger spectroscopy in the lower and the higher energy regions (LEAES and HEAES).

It is found that after the ion-bombardment the surfaces become enriched with nickel, while copper segregates on the surfaces after the annealing. Remarkable differences were observed between LEAES and HEAES on both the ion-bombarded and the annealed surfaces, from which, in combination with the difference in electrom escape length, "In-depth profile" within a few atomic layers can be estimated. It is also found that copper segregates predominantly on the top surface layer and the segregation occurs only four atomic layers (approximately 10 Å) on the annealed surfaces in all alloy samples. Whereas on the bombarded surfaces, nickel is enriched over four atomic layers. The thickness of the nickel-enriched surface layers increases with increasing copper content of the alloys in the bulk. (Japanese)

In-depth Profile of Altered Layers of Copper-Nickel Alloys Formed by Sputtering

Kuniaki Watanabe, Masao Hashiba
and Toshiro Yamashina

Surface Science, **69,** 721 (1977)

In the present paper, we described "surface composition" of outer-most surface layer over Cu–Ni alloys estimated by both lower energy Auger spectra (Cu–$M_1M_{4,5}M_{4,5}$ at 106 eV and Ni–$M_1M_{4,5}M_{4,5}$ at 101 eV) and higher Auger spectra (Cu–$L_3M_{4,5}M_{4,5}$ at 920 eV and Ni–$L_3M_{2,3}M_{2,3}$ at 712 eV) and in-depth profile of the altered layer with a new model for the selective sputtering including diffusion phenomena under ion-bombardment.

Composition of the outer-most surface layer and the thickness of the altered layer were compared by estimating from the exponential function, the step function and the Gaussian distribution function. As the results of the comparison, one can see that the step function overestimates the thickness of the altered layer for coper-rich alloys, while the Gaussian in-depth profile results in the accordant thickness of the altered layer with those estimated by a different approach, and in the concurrent values of the diffusion constant with those by the concurrent values of the diffusion constant with those by the calculation. Therefore, it is concluded that the Gaussian in-depth profile is most plausible. (English)

Instrumental Analysis of Rusts

— Stressed on Auger Electron spectroscopy —

Masahiro Seo

Corrosion Enginerring (Boshoku Gijutsu),
26, No. 6, 327 (1977)

Recently, AES (Auger Electron Spectroscopy), ESCA (Electron Spectroscopy for Chemical Analysis), APS (Appearance Potential Spectroscopy) and ISS (Ion Scattering Spectroscopy) etc. have been developed as powerful tools of the surface analysis of solids. The use of these new methods for analyses of rusts on metallic materials will throw light into the details of corrosion phenomena. This article described the methods for quantitative analyses of rusts, particularly by means of AES with aid of standard materials such as pure metal and metal oxide, and the analytical results of passive films on Fe-Cr alloy were discussed as typical examples. Finally, it was pointed out that these methods were not always almighty and should be used in parallel with other conventional methods. (Japanese)

Recovery of Hydrogen from Hydrogen Sulfide

H. Kiuchi and T. Tanaka

Transactions of the Society of Mining Engineers
of AIME, Vol. 262, Sept., 248, (1977)

The combination of the following two exothermic reactions was studied with the purpose of recovering H_2 from H_2S formed in acid leaching of sulfide ores, direct reduction of metal sulfides with H_2 or desulfurization of crude oils:

$$Pb\,(1) + H_2S = PbS(s) + H_2$$

$$PbS\,(s) + O_2 = Pb\,(1) + SO_2$$

In the kinetic study of the recovery of H_2, the reaction rate was measured by the two methods of single-stage and circulation blowing of H_2S through molten Pb in the temperature range of 550 to 750°C. The experimental results showed that the rate determining step is in the chemical reaction itself and also that this reaction is accelerated markedly by the addition of a trace of Ni, which may be responsible for the catalytic action of Ni dissolved in molten Pb. In the experiments where Pb metal was produced, PbS was oxidized in a stream of atmospheric N_2 containing 0.5 to 20 vol−% O_2 or in the same O_2 partial pressures as in N_2 though under reduced pressures in the temperature range of 400 to 800°C. It was found from these experiments that the formation of $PbSO_4$, basic sulfates and PbO are suppressable to yield Pb metal alone above 750°C and for O_2 concentrations of less than 1 vol−%. Vapor of PbS was thought to take an important part in the Pb formation mechanism, and the probability thereof was demonstrated thermodynamically. (English)

A Fundamental Study on the Reaction of Molten Lead with Hydrogen Sulfide

H. Kiuchi, T. Iwasaki and T. Tanaka

Bulletion of the Faculty of Engineering, Hokkaido
University, No. 84, 13, (1977)

The object of this study is to recover H_2 from H_2S which can be obtained from the desulfurization process of petroleum and from acid leaching or hydrogen reduction of sulfide ores. In the equilibrium between metal and H_2S, very high H_2 concentration can be thermodynamically expected. For a solid metal, however, the formation of a dense sulfide film may cause serious interference of further reaction. Such a limitation in reaction kinetics may be avoided by use of molten lead.

The reaction kinetics and mechanism have been investigated by two methods of circulation and single stage blowing of H_2S through molten lead over a temperature range of 380-790°C. In single-stage blowing, more than 80 vol-% of H_2 concentration was obtained at 790°C, as compared with 99 vol-% H_2 concentration in circulation blowing after several hours. It can be concluded that rate-determined step is in the chemical reaction itself and also that the reaction is markedly accelerated by an addition of a trace of Ni, which may be responsible for catalytic action of Ni dissolved in molton Pb.

As for the reproducing of Pb metal from PbS, the following reaction is available under low oxygen partial pressure:

$$PbS + O_2 = Pb + SO_2$$

(Japanese)

Mechanism of Electrodeposition of Copper from Cupric Pyrophosphate Solutions

H. Konno and M. Nagayama

Electrochim. Acta, **22**, 353 (1977)

Cathodic polarization curves were measured for copper in cupric pyrophosphate solutions of different concentrations and temperatures. A rotating disc electrode was used to eliminate concentration polarization. For all solutions, two potential regions are distinguishable in the polarization curve; one is less negative than a critical potential E_b around -0.75 V vs sce (Region I) and the other more negative than E_b (Region II). A weak adsorption of pyrophosphate ions and hence some inhibition of the electrodeposition of copper is expected for Region I but there is no adsorption in Region II. The exchange current density i_0 for the copper deposition was obtained by extrapolating the Tafel relation observed in Region II to the rest potential corresponding to the equilibrium potential. The following reaction mechanisms are proposed to explain the dependence of i_0 on the concentration of $Cu(P_2O_7)_2^{6-}$ and $P_2O_7^{4-}$ ions.

(A) $[P_2O_7^{4-}] < 0.09\ M$

$$Cu(P_2O_7)_2^{6-} \rightleftharpoons CuP_2O_7^{2-} + P_2O_7^{4-}$$
$$CuP_2O_7^{2-} + 2e \rightarrow Cu + P_2O_7^{4-}$$

(B) $[P_2O_7^{4-}] > 0.18\ M$

$$Cu(P_2O_7)_2^{6-} + 2e \rightarrow Cu + 2P_2O_7^{4-}$$

Apparent activation energies are estimated to be about 11 kcal/mol in both cases. (English)

Growth Rate of Hydride Layer Produced on Titanium Surface by Cathodic Polarization

T. Mizuno, T. Shindo and T. Morozumi

Corrosion Engineering (Boshoku Gijitsu),
26, 185 (1977)

The growth rate of hydride layer on the surface of titanium, which was cathodically polarized in sulfuric acid, was measured by application of the so-called etching method. The principle and the procedure of this method were rather simple; the specimen covered with a hydride layer was dissolved layer by layer by the short-time dipping in the dilute mixed solution of nitric and hydrofluoric acids, and the hydrogen-titanium ratio of the dissolved portions were determined from the weight loss of specimen and the volume of evolved hydrogen gas. From the data of a series of repeated dissolutions with a single specimen, the hydrogen concentration profile was depicted, and also the amount of hydrogen uptake and the thickness of layer were determined. The profile took a S-shaped curve and consisted of two steep and one flat branches. The results of the X-ray diffraction indicated that both of the outer steep and the flat branches corresponded to a single f.c.c. titanium hydride phase and the inner steep branch to the mixed phases of the f.c.c. and the hexagonal α-titanium. The increase of the cathodic current density and the raising of temperature both stimulated the hydrogen absorption. The rate law changed in accordance with various experimental parameters; for example, it was linear at lower current density and higher temperature, while parabolic at higher current density and lower temperature. Effects of the solution inpurities and the crystalline grain size were also investigated. (Japanese)

Adhesion of Anode Slime on Anode Surface in Electrolytic Refining of Lead

T. Tanaka

Metallurgical Transactions B of A.I.M.E.,
8B, December, 651 (1977)

In the Betts process for electrolytic refining of lead, adhesion of anode slime onto anode surface is practically very important. This investigation was undertaken to reveal dominant factors governing adhesiveness of the anode slime. The results are summarized as follows : the adhesiveness depends considerably upon the form and the physical state of impurities present in the anode, which can be classified into three types, *viz*, solid solution, preciptation, and eutectic type respectively. Solid solution types give the best adhesion. Precipitation type shows better adhesion than eutectic type. Eutectic type slides off the anode easily. The adhesion is also largely affected by the heat treatment of anode. For eutectic type, water quenching is effective to increase the adhesion. I also confirmed that the slime adhesion can be improved by the addition of elements which form intermetallic compounds with eutectic type of impurities. (English)

Computer Processing of Mössbauer Spectrum Data

M. Otsuka, H. Ohashi and T. Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 85, 81 (1977)

Computer processing was adopted to pick up significant signals from the underfined Mössbauer spectra. A program, by which smoothing and curve fitting was made possible, was devised and applied to the analysis of the Mössbauer spectra of ^{57}Fe enriched iron and other specimens. Although this processing sometimes distorted the absorption peaks, it was quite effective for elimination of noise and finding of exact positions of adsorption peaks. Availability of the processing was demonstrated by several examples obtained for ^{57}Fe enriched iron, natural iron, calcined ferric oxyhydroxides, red mud residue and its calcined product. (Japanese)