ANNUAL REPORT

1980

CORROSION RESEARCH

Materials Science and Engineering

published
by
THE CORROSION RESEARCH GROUP

FACULTY OF ENGINEERING
HOKKAIDO UNIVERSITY

NO. 9 DECEMBER 1980

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Dr. T. Ohtsuka and Miss C. Miura

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Dr. Chin-Gen Kin (China)

Students

Y. Matsumura, Y. Sera, T. Sakon, M. Masuda,
K. Azumi, I. Shintani and H. Nagao

Main subjects of research in this laboratory are concerned with surface electrochemistry of iron-groups metals and alloys. The composition and structure of anodic oxide films are investigated by means of AES and XPS. From these methodes the depth composition profiles have been determined for passive films on iron base alloys in solutions of pH ranging from acid to base. The thickness of anodic oxide films has been determined in situ with a multiangle ellipso-reflectmetry. The redox reactions on anodic oxide films on tantalum are investigated. Furthermore, a rotating ring-disc electrode technique is applied for the study of anodic dissolution of rion in acidic solutions. A gravimentric methode by means of a microbalance is being applied for the study of the cathodic reduction of anodic oxide films on copper.

In August, visiting Professor A. T. Fromfold from Auburn University, U. S. A., attended the International Conference on Transport in Nonstoichiometric Compounds held in Krakow-Mogilany, Poland, presenting a paper on the two-phase oxide growth on pure metals. In October, Prof. Sato and Assist. Prof. Seo participated in the International Conference on Metal Finishing held in Kyoto with a paper on the surface analysis of stainless steels prepared with various surface treatments. Dr. Sakashite is staying in the Institute of Physical Chemistry, FU Berlin, until February 1981.

Foreign visitors to this laboratory in 1980 are Dr. Chin-Gen Kin of Institute of Metals and Chemistry, Academy of Science for Railroad, China, as a research fellow for two years, Prof. E. Yeager of Case Western Reserve University, U. S. A., on 23–26 April. Prof. B. G. Baker of Flinders University, Australia, on 7 July, Prof. B. Jochen of Fritz-Haber-Institute, West Germany, on 9 July, Prof. A. Scheludko of the Institute of Physical Chemistry, Bulgarian Academy of Science, Bulgaria, on 1–4 October, Dr. S. R. Keown of the University of Sheffield, England, on 7 November, Mr. J. O. Nascimento Cia, Brasileira de Metalurgia e Mineracao ARAXA-MG, Brasil, on 7 November, and Prof. J. Osterwald of TU Berlin, West Germany, on 19 November.

Oral Presentation

Anodic Behaviors of Lead Electrode in Sulfuric Acid; S. Fujita, M. Sakashita and N. Sato: The 6th Hokkaido Section Meeting of JES, Jan. 1980.

Separation of Overlapped Chromium and Oxygen Auger Peaks for Quantiative Analysis; M. Seo and N. Sato: The 15th Annual Meeting of the Hokkaido Corrosion Research Assoication, Jan. 1890.

Effects of H_2S on Hydrogen Absorption into Iron; H. Murayama, M. Sakashita and N. Sato: *ibid.*, Jan. 1980.

The Temperature Dependence of Composition of Passive Films on Stainless Steels in Acidic Sulfate Solutions; M. Seo, Y. Sera, and N. Sato: Spring Meeting of JIM, April, 1980.

Structure and Composition of Anodic Oxide Films on Copper in Neutral and Weakly Alkaline Solutions; M. Seo, T. Iwata and N. Sato: The 47th Meeting of JES, April, 1980.

Measurement of Passive Film on Nickel by Three-Parameter Ellipsometry; T. Ohtsuka, N. Sato and K. E. Heusler: *ibid.*, May, 1980.

Depth-Composition Profiles of Passive Films on Iron-Binary Alloys (Fe–3Ti, Fe–5Cu, Fe–5Si); M. Seo, Y. Matsumura and N. Sato: The Annual Meeting of JSCE, May, 1980.

Hydrogen Absorption into Iron in Weakly Acidic Solutions Containing H_2S; H. Murayama, M. Sakashita and N. Sato: *ibid.*, May, 1980.

Measurement of Oxide Films on Metals by Multiple-Angyle-of-Incidence Ellipsometry; T. Ohtsuka and N. Sato: *ibid.*, May, 1980.

Change in Composition of Anodic Oxide Film on Tantalum Due to Heat Treatment in Vacuum; T. Sakon, T. Ohtsuka, M. Seo and N. Sato: The Hokkaido Section Meeting of JIM, June, 1980.

Thickness and Optical Properties of Anodic Oxide Film on Titanium in Phosphate Solutions; M. Masuda, T. Ohtsuka, M. Seo and N. Sato: *ibid.*, June. 1980.

Corrosion Cracking and Hydrogen Cracking; N. Sato: Seminar sponsored by JIM, July, 1980.

Corrosion of Metals Covered by Oxide Films; N. Sato: Summer Seminar of JSCE, July, 1980.

Tow-Phase Oxide Growth on Pure Metals; A. T. Fromhold, Jr. and N. Sato: International Conference on "Transport in Non-stoichiometric Compounds", Krakow-Mogilany, Poland, Aug., 1980.

Composional Change of Anodic Oxide Film on Tantalum Due to Heat-Treatment; T. Sakon, M. Seo, T. Ohtsuka and N. Sato: The 33th Symposium on Colloid and Interface Chemistry, Oct., 1980.

Ellipsometric Measurement of Anodic Oxide Films on Metal-Electrolyte Interface; T. Ohrsuka and N. Sato: *ibid.*, Oct., 1980.

Surface Analysis of Stainless Steels Prepared with Various Surface Treatments; M. Seo and N. Sato: International Conference on Metal Finishing, Kyoto, Oct., 1980.

On the Sputtering Rate of Passive Films on Metals; M. Seo and N. Sato: The Fall Meeting of JIM, Oct., 1980.

Titanium-Enrichment in Passive Films on Fe-3%Ti Alloy; Y. Matsumura, M. Seo and N. Sato: The Hokkaido Section Meeting of JIM, Nov., 1980.

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, S. Kobayashi, K. Fujimoto,
Y. Horii, K. Sato, H. Kumagai, M. Mukai,
Y. Saito and T. Miyamoto

Current research 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. Tamura is being on leave of absence to work with Prof. Matijevic at the Clarkson College, Potsdam, N. Y. Prof. Nagayama, Dr. Takahashi and Dr. Konno attended the 10th world congress in Metal Finishing held in Kyoto in Oct. of 1980, and at the congress Prof. Nagayama presented a paper on the composition of anodic oxide films on aluminum.

Prof. E. Yeager of CWRU, U. S. A. visited our laboratory in April, Dr. G. E. Thompson, Manchester Univ. England in Oct., and Dr. R. S. Alwitt, United Chemicon, U. S. A. in Oct.

Main subject of the research in progress are as follows :

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

(2) Geometrical Structure and Density of Porous Anodic Oxide Films on Aluminum.

Porous-type anodic oxide films are formed on aluminum in sulfuric acid solution under the conditions of different temperature, current density, and the concentration of surfuric acid to examine the morphology and the density of the films using electronmicroscopy, gravimentry and electrochemical measurements. It was found that anodizing potential, i. e. electric field in the barrier layer, is significantly responsible for the determination of the film geometry.

(3) Hydration of Porous Anodic Oxide Films on Al with Boiling Water.

The hydration process of porous anodic oxide films on Al is examined in a boiling water using the impedance measurement, gravimetry, and electrochemical measurements.

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

Ferrous ions can be oxydized by the air to form Fe(III)-hydroxide in solutions containing anions, and the rate of the oxydation is influenced by the reaction product, Fe(III)-hydroxide, as well as the anions like HPO_4^{2-}, F^-, BO_2^-, Cl^- and SO_4^{2-}. Attempts are being made to examine the effect of the coexistence of Fe(III)-hydroxide with particular anions on the kinetics of the oxydation of ferrous ions.

(5) Stability of oxide films.

The deterioration process of oxide films formed on Fe and Al are examined in neutral solutions containing fixed amounts of O_2 and anions using mainly XPS. It was found that a mono molecular layer of phosphate and chromate ions are absorbed to prevent the film form the hydration.

(6) Corrosion of iron in high temperature water.

The corrosion rate of iron in pure, high temperature water is measured by gravimetry and a polarization resistance method, and the surface oxide films formed are examined by XPS analysis.

Oral Presentation

Catalytic Decomposition of Hydrogen Peroxide on Nickel Cobaltic Oxides; H. Takahashi and E. Yeager: The 6th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1980.

Stability of Oxide Films on Iron in Neutral Solutions Containing Various Electrolyte Anions; H. Konno, M. Kawai and M. Nagayama: The 15th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1980.

Measurement of Oxygen Reduction on Powdery Metal Oxides with Rotating Cavity Ring-Disk Electrode; H. Takahashi and E. Yeager: The 1979 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Jan. 1980.

Decomposition Kinetics of Hydrogen Peroxide on Ni-Co Oxides in Alkaline Solutions; H. Takahashi and E. Yeager: The 47th Annual Meeting of the Electrochem. Soc. of Japan, April 1980.

Breakdown of Anodic Oxide Films on Iron with Electrolyte Anions; H. Konno, M. Kawai and M. Nagayama: *ibid.*, April 1980.

Anodizing of Aluminum in a Neutral Phosphate Solution and the Chemical Structure of the Formed Oxide Films; K. Fujimoto, H. Takahashi, H. Konno and M. Nagayama: The 61st Meeting of the Metal Finishing Soc. Japan, May 1980.

Electrodeposition of Chromium from $CrCl_3$-Clycine Solution; H. Konno, M. Nagayama and K. Yokoyama: *ibdi.* May 1980.

Effects of Anodizing Potential on the Geometrical Structure of Porous Anodic Oxide Films on Aluminum; K. Ebihara, H. Takahashi and M. Nagayama: The 1980 Summer Meeting of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., Aug. 1980.

Hydration of the Barrier-Type, Anodic Oxide Films on Aluminum; S. Kobayashi, H. Konno, H. Takahashi and M. Nagayama: *ibid.* Aug. 1980.

Oxygen Electroreduction Catalysis with spinels; H. Takahashi, W. Aldred, P. Bindra and E. Yeager: The 31st Meeting of the I. S. E., Sept. 1980.

XPS Studies on Barrior Oxide Films Formed on Aluminum in Neutral Borate and Phosphate Solutions; H. Konno, S. Kobayashi, K. Fujimoto, H. Takahashi and M. Nagayama: The 10th World Congress on Metal Finishing, Oct. 1980.

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

K. Kurokawa, Y. Takeda, K. Kitazima, T. Kodama,
M. Shindo, M. Morikawa and N. Yoshinaga

This laboratory is concerned with fundamental studies on the high-temperature corrosion of metals and alloys in oxygen, sulfur, and their mixed oxidant atmospheres as well as the related diffusion phenomena. The research subjects in progress are as follows:

(1) High-Temperature Sulfidation: Sulfidation of Fe–Cr alloys were investigated by using of TGM, X-RAY, SEM, and EPMA to reveal the grain boundary attack for the intermediate alloys sulfidized at 1073 K and $P(s_2)=10^{-5}$ Pa. There was, however, copious internal sulfidation in the Fe–Mn alloys sulfidized at temperatures of 973 to 1273 K. The sulfidation in vestigations are now being directed to the ternary alloys of Fe–Cr–Al and Fe–Mn–Cr systems.

(2) High-Temperature Oxidation: Oxidation studies were concentrated to elucidate the growth mechanism of the duplex scales formed on Co–Mn and Co–Fe alloys at elevated temperatures.

(3) High-Temperature Corrosion in mixed Oxidants: Corrosion behaviors of iron and its alloys containing alumium and manganese were investigated in the Ar-diluted SO_2 gas mixtures at elevated temperatures and revealed the morphologies of the external scale and corrosion kinetics. It was considered that the direct reaction of SO_2 gas molecules to metal should be ascribed to the growth of the composite sulfide and oxide scales with lamellar structures, which obey the linear kinetics.

(4) Surface Coating: The aluminizing treatment of Ta and

Nb recealed to improve oxidation resistance of these refractory metals at high-temperatures, which is due to the formation of the $TaAlO_4$ ahd $NbAlO_4$ phases in the external scale. The D. C. assisted glow discharge was applied to overlay thick carbon on the metal surfaces of iron and tantalum, to give an amorphous carbon layer with about 5 μm in thickness by 30 min coating.

(5) Inter-diffusions in Alloys and Oxides: To gain the fundamental informations on diffusion phenomena, several diffusion couples were investigated for the α-phase of Co-Sb, Co-Sn and Cu-Zn systems. In relation to the oxidation of the aluminium surfacetreated tantalum, mutual reactivity between Ta_2O_5 and Al_2O_3 pellets was investigated at 1673 to 1773 K.

Professor Nishida participated in The 9th Symposium on the Reactivity of Solids, Sept. 1-6, 1980, held in Cracow, Poland and presented the paper entitled" High-Temperature Sulfidation of Some Fe-Mn alloys under Low Sulfur Pressures", and then attended to The 10th World Congress on Metal Finishing, Oct. 12-17, 1980, Kyoto, Japan and presented the paper entitled "Calorizing of Ta sheets and their Oxidation Behavior".

Oral Presentation

Sulfidation Behavior of Alloys in Low Sulfur Pressure; T. Narita and W. W. Smeltzer: The 15th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan, 1980.

Sulfidation of Fe-Mn Alloys under Low Sulfur Pressures (Part III); Y. Takeda, T. Narita and K. Nishida: The Spring Meeting of the Japan Institute of Metals, April, 1980.

Sulfidation of Fe-25Cr Alloys Containing Various Amount of Aluminum at 1073 K; T. Narita and W. W. Smeltzer: *ibid.*, April, 1980.

Inter-diffusion in α Phases of a Ni-Sn System; T. Yamamoto, T. Takashima and K. Nishida: *ibid.*, April, 1980.

Sulfidation Behavior of Fe-Cr Alloys at 1073 K and $P(S_2)=10^{-5}$ Pa; T. Narita, M. Ikeda and K. Nishida: The Hokkaido Section Meeting of JIM, June, 1980.

The Effect of Pre-oxidation on the High-Temperature Corrosion of Fe-3%Al Alloys in the Ar-SO_2 Atmosphere; K. Kurokawa, T. Narita and K. Nishida: *ibid.*, June, 1980.

Inter-diffusion in α Phase of a Co-Sb System; T. Takashima, T. Yamamoto and K. Nishida: *ibid.*, June, 1980.

High-Temperature Sulfidation of Some Fe-Mn Alloys under Low Sulfur Pressures; K. Nishida and K. Godlewski: The 9th International Symposium on the Reactivity of Solids, (Poland) Sept., 1980.

Calorizing of Ta Sheets and their Oxidation Behavior; K. Nishida and M. Hachinohe: The 10th International Congress on Metal Finishing, Oct., 1980.

Computer Simulation of Alloy Oxidation (Part I, The Co-Fe-O System); T. Narita, N. Suzuki, W. W. Smeltzer and K. Nishida: The Fall Meeting of Japan Institute of Metals, Oct., 1980.

Sulfidation Behavior of Fe-Mn Alloys under Low Sulfur Pressures (Part IV); Y. Takeda, T. Narita and K. Nishida: *ibid.*, 1980.

Sulfidation of Fe-Cr Alloys at 1073 K and $P(S_2)=10^{-5}$ Pa (Part II); T. Narita, M. Ikeda and K. Nishida: *ibid.*, Oct, 1980.

High-Temperature Corrosion of Fe-Al Alloys in the Ar-SO_2 Atmospheres (Effect of Pre-Oxidation); K. Kurokawa, T. Narita and Nishida: *ibid.*, Oct, 1980.

Inter-diffusion in α Phase of a Co-Sb System; T. Yamamoto, T. Takashima and K. Nishida: *ibid.*, Oct, 1980.

Porosity Variation during Hydrogen Reduction of Iron Oxides Containing Different Metal Oxides with and without Sintering Treatment; Y. Suzuki, M. Yamamoto, T. Kotanigawa and K. Nishida: The Fall Meeting of Iron and Steel Institute of Japan, Oct., 1980.

Fundamental Aspects of Sulfidation Behaviors of Fe-Cr Alloys under Low Sulfur Pressures; T. Narita and K. Nishida: Annual Conference of the Japan Society of Corrosion Engineering, Oct., 1980.

Diffusional Analyses of Sulfide Scale Growth on Fe-Cr Alloy; T. Narita, W. W. Smeltzer and K. Nishida: *ibid.*, 1980.

High-Temperature Oxidation of Co–Mn Alloys; S. Hashimura, T. Narita and K. Nishida: The Fall Meeting of Hokkaido Section of JIM, Nov., 1980.

High-Temperature Corrosion of Fe–Mn Alloys in the Ar–SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: *ibid.*, Nov., 1980.

ELECTROMETALLURGY LABORATORY

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

Students

S. Ohkubo, M. Murakami, S. Ajimura, M. Itatsu,
S. Mikami, H. Hanzawa 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°C to 800°C. The electric conductivity of these molten salts and volatile composition from the melts are being measured in this temperature range for cell design and operation analysis.

(2) Various bipolar electrode are developed to remove electrochemically heavy metals from the waste water on metallurgical processes and fundamental functions of the cells are being studied

(3) In the field of corrosion inhibitors the study has been concentrated on mechanisms of inhibition action of benzotriazole and its derivatives for different kinds of metals and alloys using electrochemical techniques as well as spectroscopic analyses, such as the infrared, the visible and the ultraviolet spectrophotometry.

(4) The resistometric measurements for continuous determination of the corrosion rate of metals in molten salts are being undertaken in alkali nitrate melts of 350°C to 450°C. The immersion tests are being carried out in the same melts.

(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.

Oral Presentation

Rotating Bipolar Electrode Cell with Self-pumping Action; T. Sasaki and T. Ishikawa: The 6th Hokkaido Section Meeting of Electrochem. Soc. of Japan, Jan. 1980.

Effects of Micro-vibration on the Corrosion of Mild Steel in Neutral Solutions; M. Murakami and T. Ishikawa: 15th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 1980.

Corrosion Inhibition of Aluminum Brass by Organic Corrosion Inhibitors; T. Notoya and T. Ishikawa: The 1980 Winter Meeting of the Hokkaido Section of the Japan Chemical Society, Jan. 1980.

A Technique for Maintaining Electrode Distances to Anodic Surface Consumption of Bipolar Electrode Cell; S. Ohokubo and T. Ishikawa: The 47th Annual Meeting of the Electrochem. Soc. of Japan, April 1980.

Application of Rotating Bipolar Electrode Cell to Electrochemical Reduction of Potassium Dichromate and Copper Sulfate; T. Sasaki, T. Shigematsu and T. Ishikawa: *ibid.*, April 1980.

Corrosion Inhibition of Iron and Brasses by Benzotriazole Derivatives; T. Notoya and T. Ishikawa: '80 Spring Meeting of the Japan Society of Corrosion Engineering, May 1980.

Corrosion Inhibitors for Solar Energy Systems; T. Notoya and T. Ishikawa: The Hokkaido Section Meeting of the Japan Institute of Metals, June 1980.

On the Electrowinning of Liquid Aluminum from Aluminum Chloride; T. Ishikawa: Research Commitee on Aluminum New Smelting Process, Japan Aluminum Federation, July 1980.

Benzotriazole Derivatives as Corrosion Inhibitors for Iron; T. Notoya and T. Ishikawa: The 1980 Summer Meeting of the Hokkaido Section of the Japan Chemical Society, July 1980.

On a Method for Evaluation of the Function of Rotating Bipolar Electrode Cell; T. Sasaki, K. Orita and T. Ishikawa: The 1980 Fall Meeting of Electrochem. Soc. of Japan, Oct. 1980.

Electrowinning of Liquid Aluminum by using Funnel-Pile Type

Bipolar Electrode Cell (Part 7) A Technique for Maintaining Electrode Distances to Anode Surface Consumption during Electrolysis; S. Ohokubo, S. Konda and T. Ishikawa: 14th Symposium on Molten Salt Chemistry, Nov. 1980.

Studies on the Properties of High Temperature Chloride Melts containing Aluminum Chloride (Part 4) Determination of Volatile Compositions from Various Solvent Melt Systems; S. Ajimura, S. Konda and T. Ishikawa: *ibid.*, Nov. 1980.

Industrial Electrolysis of Aluminum Chloride —Potentials and Problems—; T. Ishikawa: 28th Symposium on Non-Ferrous Metallurgy, Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Nov. 1980.

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

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

Students

N. Tsucida, K. Funaki, R. Togashi, K. Ise, H. Ōtomo,
M. Ōhara and Y. Nakai

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) Processes for hydrogen production without using fossil fuels.

i) Thermochemical splitting of hydrogen sulfide.

Thermochemical splitting of H_2S by the following two combination reaction is being investigated

$$\begin{array}{l} MS_x + H_2S = MS_{x+1} + H_2 \\ MS_{x+1} = MS_x + S^\circ \\ \hline H_2S = H_2 + S^\circ \end{array}$$

ii) Pyrohydrolysis of metal chlorides.

This reaction has recieved much attention not only in the metallurgical field but also in the energy field owing to thermochemical splitting of water.

iii) Hydrogen production by using water and sulfur or sulfur compounds. Reaction between steam and a metal sulfide such Ag_2S, CaS, and FeS are being carried out within the temperature range 700~1,000°K for the purpose of hydrogen production from water.

Production of hydrogen according to the following reactions are in progress

$$2H_2O + SO_2 = H_2SO_4 + H_2$$

$$4H_2O+S=3H_2+H_2SO_4$$
$$4H_2O+H_2S=4H_2+H_2SO_4$$

(2) Application of hydrogen to the treatment of metallurgical raw materials.

i) Reduction of metal sulfides with hydrogen.

Kinetic studies on the direct reduction of sulfide ores with hydrogen are being made.

ii) Reduction of metal sulfates with hydrogen.

As hydrogen reduction of metal sulfates proceeds under a relatively low temperature as 300°C, the application of waste heat to metallurgy will be expected.

iii) Reduction of metal sulfates or chlorides with hot gas from pyrohydrolysis of ferrous chloride.

Effect of HCl gas on the reduction of Cu, Ni, and Co sulfates and chlorides are being examined.

(3) Removal of arsenic from spent copper electrolyte solution by hydrogen pressure reduction.

Removal of copper and arsenic from spent copper electrolyte solution by hydrogen pressure reduction in an autoclave has been studied as a purification technique for the electroclyte. The purpose of this study is to replace the conventional process which includes stripping of metals from the electrolyte using insoluble anodes and is a power consuming process.

Oral Presentation

Metal Sulfides and Hydrogen; T. Tanaka, H. Kiuchi and R. Shibayama: The Hokkaido Section Meeting of JIM, Jan., 1980.

Fixation of Sulfur by the thermochemical splitting of Hydrogen Sulfide (II); T. Tanaka and H. Kiuchi: Research committee for Fixation of Sulfur, Min. Met. Inst. Japan, Jan., 1980.

Thermochemical Splitting of H_2S by Using Solid Metal (II); H. Kiuchi, I. Nakamura and T. Tanaka: The 1980 Winter Meeting of the Hokkaido Section of the JSAC and JCS, Feb., 1980.

Pyrohydrolysis of Metal Chlorides; R. Shibayama, N. Tsuchida and T. Tanaka: *ibid.*, Feb. 1980.

Treatment of Arsenic Bearing Solutions. —Removal of Arsenic from Copper Smelters and Geothermal Power Plants—; T. Nagai, M. Kobayashi and K. Higashioka: Meeting on Mineral Processing and Metallurgy, The Hokkaido Section of Min. Met. Inst. Japan, March 1980.

Recoveries of Hydrogen and Elemental Sulfur from Hydrogen Sulfide; H. Kiuchi, T. Iwasaki and T. Tanaka: *ibid.*, March 1980.

A Study for the Effective Utilization of Hydrogen Sulfide (VI); H. Kiuchi, I. Nakamura and T. Tanaka: Annual Meeting of Min. Met. Inst. Japan, April 1980.

Fundamental Studies on the Pyrohydrolysis of Metal Chlorides (III); R. Shibayama, N. Tsuchida and T. Tanaka: *ibid.*, April (1980).

Removal of Arsenic in the Hot Waste Water from Geothermal Power Plants by Hydrated Zirconium Oxide; T. Nagai and R. Togashi: *ibid.*, April 1980.

Action of Metal Sulfide on the Thermal Decomposition of Hydrogen Sulfide (IV): H. Kiuchi, K. Funaki and T. Tanaka: The Hokkaido Section Meeting of JIM and ISIJ, June 1980.

Recovery of Hydrogen and Elemental Sulfur from Hydrogen Sulfide (IV); H. Kiuchi, K. Funaki and T. Tanaka: The Spring Meeting of the Hokkaido Section of the Min. Met. Inst. Japan, June 1980.

Fundamental Studies on the Pyrohydrolysis of Metal Chlorides (IV); R. Shibayama, N. Tsuchida and T. Tanaka: *ibid.*, June 1980.

Removal Arsenic in the Hot Waste Water from Geothermal Power Plants; R. Togashi and T. Nagai: *ibid.*, June 1980.

Recovery of hydrogen from Hydrogen Sulfide with Metals or Metal Sulfides; H. Kiuchi, I. Nakamura, K. Funaki and T. Tanaka: The 3rd World Hydrogen Energy Conference, Tokyo, June 1980.

Fixation of Sulfur by the Thermochemical Splitting of Hydrogen Sulfide (III) —Thermochemical Splitting of Hydrogen Sulfide with Nickel Sulfide—; T. Tanaka, H. Kiuchi and K. Funaki:

Research Committee for Fixation of Sulfur, Min. Met. Inst. Japan, July 1980.

Recovery of Hydrogen Sulfide with Metal Sulfides (III); H. Kiuchi, K. Funaki and T. Tanaka: The 1980 Summer Meeting of the Hokkaido Section of the Japan Chem. Soc., Aug. 1980.

Recovery of Hydrogen and Elemental Sulphur from Hydrogen Sulfide (V); H. Kiuchi, K. Funaki and T. Tanaka: The Fall Meeting of the Hokkaido Section of the Min. Met, Inst. Japan, Nov. 1980.

Fundamental Studies on the Reaction between Metal Chlorides and Steam; R. Shibayama, N. Tsuchida and T. Tanaka: *ibid.*, Nov. 1980.

Hydrogen Reduction of Copper Sulphate Solution in High Acid Level; R. Togashi and T. Nagai: *ibid.* Nov. 1980.

Removal of Arsenic from Hot Waste Water from Geothermal Power Plants; T. Nagai and R. Togashi: *ibid.*, Nov. 1980.

Use of Hydrogen Sulphide as a Source of Hydrogen; H. Kiuchi, K. Funaki and T. Tanaka: The 4th Joint Meeting Min. Met. Inst. Japan and Amer. Inst. Min. Met. Eng. Nov. 1980.

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

T. Shindo, M. Otsuka, T. Itaya, T. Sato, K. Itoki,
K. Ogura, T. Onishi and S. Doi

Dr. Moriya went on leave in November 1980 to work with Prof. M. B. Ives at the McMaster University, Hamilton, Ontario, Canada.

Research is currently being carried out on several physico-chemical problems including corrosion. The main subjects of the research are as follows:

(1) Mössbauer absoption spectra of iron were measured in situ during high temperature oxidation. Analyzing the spectra, both oxidation rate constants and the reaction products were determined. The oxidation of iron proceeded in two distinct stages first α-Fe to Fe_3O_4 and second Fe_3O_4 to α-Fe_2O_3. The oxidation in the first stage followed a first order rate law and in the second stage obeyed a parabolic rate law. This suggests that the first stage reaction is not a simple diffusion-controlled process. Lattice dynamical properties of the intermediate Fe_3O_4 was found to be different from standard Fe_3O_4 samples.

(2) The formation of superparamagnetic (spm) α-FeOOH and its aging characteristics were investigated by the Mössbauer spectroscopic method. The spm α-FeOOH was formed by neutralizing $FeSO_4$ solutions with NaOH, and oxidizing with air. The formation of this material was possible only with low $FeSO_4$ (<0.1 mol/l) concentration and temperatures below 50°C. By aging in aqueous solutions fine grains of spm α-FeOOH grew and transformed to antiferromagnetic α-FeOOH. The growth rate of spm α-FeOOH

followed a first order rate law. From this, it was concluded that spm α-FeOOH can be formed by corrosion of iron and steels in natural environments.

(3) The development of a system for electrode impedance measurement, which is equipped with a micro-computer system for on-line data-processing, was completed. This system can be used for measurements over wide frequency range (10^{-3} to 10^4 Hz) with both FORTRAN and BASIC languages. The system was used to measure impedance of titanium, zirconium and Hastelloy-C electrodes during anodizing in H_2SO_4 solutions. The results are now being considered.

(4) Diffusion of hydrogen absorbed in zirconium during cathodic polarization was investigated. After hydride was formed for a given period, cathodic polarization was continued in a solution of D_2SO_4 in D_2O. The experiment was also conducted first with D_2SO_4 in D_2O, and second H_2SO_4 in H_2O. Then distribution of deuterium in the zirconium was determined by a nucleo-chemical method with a Cockcroft-Walton accelerator. Some peculiar diffusion phenomena were observed, and the possible mechanism of hydrogen diffusion is being considered.

Further, hydrogen absorption in titanium during cathodic polarization was investigated. The growth rate of titanium hydride was found to depend on both pH and hydrogen over-voltage. Needle-like hydride was observed at the boundary region between plate-like hydride and metal matrix. A new method has been proposed for the prevention of the hydriding by anodic pulse oxidation.

(5) Investigation of hydrogen absorption was continued for iron-titanium alloys with various compositions. The rate of hydrogen absorption depended on the composition of the alloys and it was maximum at a composition near $FeTi_{1.2}$. With this alloy, the initial rate of hydrogen absorption and susceptibility to impurities in hydrogen gas were superior. The effects of additive elements were also examined.

(6) Deuterium retention in metals was investigated with a Cockcroft-Walton accelerator. Fe, Ni, Mo, Pd, Ti, Zr and W tragets were bombarded with 100 keV deuteron beams at -196, -80,

and 20°C, and changes in neutron counts were measured with a BF_3 counter. Fe, Ni, Mo, and Pd behaved differently from Ti, Zr and W.

(7) Recovery of uranium from simulated leaching solutions by anion exchange resin was investigated. The exchange has been considered to occur in the form of uranyl complex ions, such as $UO_2(SO_4)_2^{2-}$ or $UO_2(SO_4)_3^{4-}$. Maximum value for isothermal exchange, i. e. resin loading and the rate constant was obtained as functions of pH, temperature and concentration of Fe(III) impurity.

Oral Presentation

Effect of pH on Growth of Zirconium Hydride under Cathodic Polarization; T. Sato, T. Mizuno and T. Morozumi: The 6th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1980.

On-line Data Processing in Corrosion Measurements; M. Moriya, M. Kitaichi, F. Miyashita and T. Morozumi: *ibid.*, Jan. 1980.

Study of Thermal Transformation of Iron Oxide Hydroxide in Steam; T. Itaya, M. Otsuka, H. Ohashi and T. Morozumi: The 15th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 1980.

Mössbauer Spectroscopic Study of Superparamagnetic Components in Iron Rusts; M. Otsuka, H. Ohashi and T. Morozumi: The 1980 Winter Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., Feb. 1980.

Effect of Hydrofluoric Acid on Dissolution of Microspherical Uranium Dioxide; H. Ohashi, S. Nakao, H. Ogawa and T. Morozumi: *ibid.*, Feb. 1980.

Effect of Alloy Composition on Hydrogen Absorption Property of Fe–Ti Alloy; J. Masuko, T. Mizuno and T. Morozumi: *ibid.*, Feb. 1980.

Rate of Dissolution of Uranium Dioxide in Aqueous Solutions of Nitric/Hydrofluroic Acid; H. Ohashi, S. Nakao, H. Ogawa and T. Morozumi: The Annual Meeting of the Atomic Energy

Society of Japan, Mar. 1980.

Study of Formation of Superparamagnetic Iron Rust Components by Mössbauer Spectroscopy; M. Otsuka, T. Itaya, H. Ohashi and T. Morozumi: The Annual Meeting of Japan Society of Corrosion Engineering, May 1980.

Measurement and Analysis of Electrode Impedance with Microprocessor-Controlled System; M. Moriya, M. Kitaichi, F. Miyashita and T. Morozumi: *ibid.*, May 1980.

Effect of pH on Formation of Hydride Layer on Titanium Surface; T. Sindo and T. Morozumi: *ibid.*, May 1980.

A Method of Measurement of Oxidation Rates of Iron; H. Ohashi: Seminar on Corrosion and Oxide Film Sponsored by the Corrosion Research Association in Hokkaido, July 1980.

Investigation on Kinetics of Growth of Superparamagnetic α-FeOOH; T. Itaya, M. Otsuka, H. Ohashi and T. Morozumi: The 1980 Summer Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., July 1980.

Measurement of Oxidation Rates of Iron and Steels by Mössbauer Spectroscopy; H. Ohashi. M. Otsuka and T. Morozumi: The 27th Symposium on Corrosion and Protection of the Japan Society of Corrosion Engineering, Oct. 1980.

Isotopic Effect on Hydrogen Absorption Behavior of Fe-Ti Alloys; T. Mizuno, J. Masuko and T. Morozumi: The Fall Meeting of Japan Institute of Metals, Oct. 1980.

PHYSICAL METALLURGY LABORATORY

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

Students

S. Ohnuki, S. Maruyama, S. Wazima, T. Ebe, T. Kato,
T. Katayama, Y. Takahashi and H. Ohmori

Newly developed high voltage electron microscope (HVEM) of 1300 kV was installed this year. The HVEM is specially designed for studing irradiation damages in metals and alloys which will be used for future breader or fusion reactor. The HVEM is equipped with the dual beam irradiation facilities, by which a simulatanious irradiation of electron and helium ion can be performed in a similar or an accelarated condition as in the reactor condition. Environmental cell is also provided for in situ experiments of gasmetal reaction, biological studies and others. Ultra high clean vacuum up to 10^{-6} Pa and high resolution power up to 0.144 nm can be achieved in this HVEM so as to give a powerful tool for microstrutural studies in various fields such as physical, chemical and biological science in addition to the irradiation study on materials.

In this laboratory radiation induced segregation, phase instability and void formation in various metals and alloys have been pursued extensively in these years as a part of the national research project of fusion reactor. Corrosion related studies include the stochastic approach for pitting corrosion and statistical analysis of stress corrosion cracking failure times which could be used to evaluate the life time of materials against corrosion. High speed straining electrode apparatus incorporated in the high temperature and pressure water autoclave was introduced to study the mechanism of stress corrosion cracking of stainless steels in the BWR environment.

In September, Prof. Takeyama and Dr. Takahashi attended the 6th International Conference on HVEM held at Antwerp, Belgium, to present a paper on Radiation Induced Segregation in Electron Irradiated Copper Alloys. Before and after the conference, he visited Max-Planck-Institut für Metallforschung, Institut für Physik West Germany, Oxford University and AERE, Harwell, England, Centre D5Etudes Nucleaires de Saclay and the French A. E. C. Research Center, France. In May, Assist. Prof. Shibata attended the 4th International Conference on Titanium held at Kyoto, Japan, to present a paper of Stress Corrosion Cracking of Ti-N Alloys in Iodine-Methanol. In December, Prof. Takeyama and Dr. Ohnuki participated in the Japan-US Seminar on Materials, Results of Irradiation Work and Exploration of Ferritic Status held in Tokai, Japan, to present a paper entitled Study of Segregation in Alloys Irradiated by Ions and Electrons. In November, Dr. Takahashi came back after staying one year and three months at Max-Planck-Institut für Metallforschung, Institut für Physik, Stuttgart, West Germany.

Oral Presentation

Irradiation Induced Segregation; T. Takeyama: Research Meeting on Atomistic Level Structure of Lattice Defects by High Resolution Electron Microscopy, Jan., 1980.

Probability Distribution of Stress Corrosion Cracking Failure Times of Type 316 Stainless Steel; T. Shibata and T. Takeyama: The 15th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1980.

Application of "Analytical Electron Microscopy" to Metallurgy; T. Takeyama, S. Ohnjki, G. Sato and S. Mochizuki: The Hokkaido Section Meeting of Japan Society of Electron Microscopy, Feb., 1980.

Corrosion Probability and Stress Corrosion Probability; T. Shibata: The 25th Japan National Symposium on Stength, Fracture and Fatigue, April, 1980.

Irradiation Induced Segregation in Electron Irradiated Cu Alloys (II); S. Ohnuki and T. Takeyama: The Spring Meeting of the Japan Institute of Metals, April, 1980.

Orientation Pits of Ti Formed by Potentiostatic Electrolysis; T. Shibata and T. Takeyama: *ibdi.*, 1980.

Probability Distribution of Stress Corrosion Cracking Failure Times of Type 316 Stainless Steel; T. Shibata and T. Takeyama: Annual Conference of the Japan Society of Corrosion Engineering, May, 1980.

Stress Corrosion Cracking of Ti-N Alloys in Iodine-Methanol; T. Shibata, T. Takeyama and K. Kurokawa: 4th International Conference on Titanium, May, 1980.

Observation of Irradiation Induced Segregation by EDX; T. Takeyama, S. Ohnuki, G. Sato and S. Mochizuki; Japan Society for Electron Microscopy, June, 1980.

Pit Generation of 17Cr Ferritic Stainless Steels; T. Shibata, T. Takeyama and Y. Tanaka: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute, June, 1980.

Hydrogen Indeuced Microcracks of Iron and Steel; T. Takeyama: Seminar on Corrosion Cracking and Hydrogen Embrittlement sponsored by the Japan Institute of Metals, July, 1980.

Analysis of stress Corrosion Cracking Condition by Straining Electrode; T. Shibata: *ibid.*, July, 1980.

Development of Ultra High Temperature Apparatus for Deformation and High Temperature Deformation Behavior; T. Takeyama, G. Tomita, H. Murakami, T. Yanagisawa and S. Wagima: Symposium for High Melting Metals, July, 1980.

Stress Corrosion Cracking and Straining Electrode; T. Shibata: The 33rd Corrosion and Prevention Symposium, Sept., 1980.

Radiation Induced Segregation in Electron Iradiated Copper Alloys; T. Takeyama, S. Ohnuki and H. Takahashi: 6th International Conference on HVEM, Sept., 1980.

Effect of Irradiation on Phase Stability; T. Takeyama: Centre D'Etudes Nucleaires de Saclay, Sept., 1980.

Stability of Micro Crack due to Precipitation of Hydrogen in Iron and Steel; T. Takeyama: The French A. E. C. Research Center, Sept., 1980.

Analysis of Electrochemical Conditions of Stress Corrosion Cracking of Stainless Steels by Straining Electrode; T. Shibata and T. Takeyama: The Fall Meeting of the Japan Institute of Metals, Oct., 1980.

Irradiation Induced Segregation of Electron Irradiated Cu–Ni Alloys; S. Ohnuki and T. Takeyama: *ibid.*, Oct., 1980.

Effect of Composition on Void Formation of Electron Irradiated Cu–Ni Alloys; H. Ohgami, H. Takahashi, S. Ohnuki and T. Takeyama: *ibid.*, Oct., 1980.

Development of Ultra High Temperature Apparatus for Deformation and High Temperature Deformation Behavior of Mo; S. Wagima, G. Tomita and T. Takeyama: *ibid.*, 1980.

Void Formation in Electron Irradiated Fe–Mn Alloys; S. Maruyama, S. Ohnuki and T. Takeyama: *ibid.*, Oct., 1980.

Study of Segregation in Alloys Irradiated by Ions and Electrons; T. Takeyama, S. Ohnuki and S. Maruyama: Japan-US Seminar on Materials, Results of Irradiation Work and Exploration of Ferritic Status, Oct., 1980.

Phase Stability of Alloys under Irradiation Condition; T. Takeyama, H. Takahashi and S. Ohnuki: Research Meeting on Fusion Reactor First Wall Materials, Nov., 1980.

Radiation Induced Segregation in Ferritic Steels; T. Takeyama, H. Takahashi and S. Ohnuki: Research Meeting on Fusion Reactor First Wall Materials, Dec., 1980.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

H. Tsushima, T. Terada, T. Nakamura, Y. Kawahara,
H. Ishida, K. Ōkubo, T. Narita, N. Minami,
H. Hasegawa, K. Watanabe
and T. Kanazawa

In this laboratory basic researches are concerned on mechanical and thermal properties of cast iron, and applied researches are on failure analysis of machine members.

Professor Nagaoka attended the 8th JFS symposium on Heat Resistance of Castings Nov. 3, 1980 held in Sendai to give a keynote speech and a lecture on growth mechanism of cast iron.

Subjects of the research in progress are as follows:

(1) As a step of the research on bending strength of cast iron circular plate, effect of radial ribs was examined experimentally. The circular plate was strengthened remarkably by radial ribs. The effect was mainly attributed to the increase of thickness of the plate at the center with the increase of number of ribs. The results was compared with the effect of annular ribs which was analyzed formerly with FEM.

(2) According to a fracture criterion of gray cast iron proposed in this laboratory the depth of critical stress in the member was related to the size of graphite eutectic cell of the cast iron. In order to confirm the criterion rupture tests were carried out on beams and notched bars with specimens controlled the finess of graphite eutectic cell by rapid cooling in solidification. The results showed that the finer the cell the higher the rupture strength, but

the effect was not so much.

(3) Tests on low cycle fatigue of cast iron was started in this laboratory and rate of crack growth was observed with a optical microscope. Though the fatigue crack grew stepwise the whole curve was approximated by a hyperbolic line.

(4) Mechanical behaviour of sintered iron was examined experimentally in tension, compression and bending. Rupture strength was affected by the non-elastic stress-strain relation of the material, but the behavior was almost elastic in liquid nitrogen temperature. Some mechanical analyses were performed with numerical functions approximated on stress strain relation.

(5) Growth of cast iron was tested in air with oxygen concentration changed by a oxygen pump. Acceleration of growth with low concentration of oxygen was observed not only in the transformation temperature range but also in the austenite region. The results suggested that the effect of oxygen in air on the growth of cast iron might be examined in the simple thermal condition of austenite region.

(6) Some tests were performed on the effect of size of graphite nodules on the impact strength of nodular graphite cast iron. The finer the graphite nodules the lower the transition temperature, though the lower the impact energy at upper shelf.

(7) Tensile tests of copper tube soldered to brass castings for heat supplying showed that the strength of copper tube decreased as a half of that before the soldering. Therefore the mechanical quality of soldering is defined by the strength of copper tube softened by recrystalization occurred during the soldering.

Oral Presentation

Effect of Circumferential Ribs on the Bending Strength of Cast Iron Circular Plate; T. Noguchi and K. Nagaoka: The 97th Grand Lecture Meeting of the Japan Foundrymen's Society, May 1980.

Effect of Oxygen Concentration in Air on the Growth Characteristics of Flake Graphite Cast Irons; M. Sōma and K. Nagaoka:

The 97th Grand Lecture Meeting of the Japan Foundrymen's Society, May 1980.

Bending and Notch Strength of Cast Iron with Fine Graphite Eutectic Cell; T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society, June 1980.

Effect of Shape and Dimension of Specimen on the Tensile Strength of Cast Iron; T. Noguchi, Y. Kawahara and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society, June 1980.

On the Mechanical Properties of Grown Cast Iron; M. Sōme and K. Nagaoka: The 98th Grand Lecture Meeting of the Japan Foundrymen's Society, Nov. 1980.

Growth and Heat Resistance of Cast Iron; K. Nagaoka: The 8th Symposium of the Japan Foundrymen's Society "Heat Resistance of Castings", Nov. 1980.

Failures of Machine Members and Prevention; K. Nagaoka: The 4th Course of Lecture in Hakodate District by the Hokkaido Section of the Japan Mechanical Engineers Society, Oct. 1980.

Failure Analysis of Machine Elements; K. Nagaoka: The Coruse of Lecture on Engineerings by the Press Nikkan Kogyo, Nov. 1980.

Mechanism of Homogeneous and Heterogeneous Anodic Dissolution of Metals

N. Sato

Proceedings of The 2nd Japan-USSR Corrosion Seminar;
(Homogeneous and Heterogeneous Anodic Dissolution
of Metals and Their Inhibition) October 23-26,
1979, Tokyo, Published by JSCE,
May 1980, pp. 35-60

The dissolution mechanisms in the active state are grouped into three categories; the acid-catalyzed aniono-ligand mechanism, the base-catalyzed hydroxo-ligand mechanism, and the water-catalyzed aquo-ligand mechanism. Anions either accelerate or inhibit anodic metal dissolution in the active state by directly incorporating or interacting with reaction intermediates adsorbed on the metal surface. In general, the electrosorption of electrolyte constituents on the metal surface plays a decisive role in the mechanism of active metal dissolution. The passive dissolution takes place in the presence of passive surface films and its rate is controlled by the potential drop at the film-electrolyte interface. Heterogeneous dissolution results when more then one state of metal dissolution are formed at different sites on the same metal surface. Mostly, the active, transpassive, or brightening dissolution takes place locally on the passive metal surface. (English)

Corrosion Inhibition of Copper with Potassium Octylhydroxamate

T. Notoya and T. Ishikawa

Bulletin of the Faculty of Engineering, Hokkaido
University, No. **98,** 13 (1980)

The inhibitive effect of potassium octylhydroxamate (P-OHO) on the corrosion of copper in both acidic and neutral NaCl solutions was investigated by means of corrosion tests, electrochemical polarization and infrared spectroscopy. P-OHO was found to be a good inhibitor in chloride environments. The inhibition efficiency was determined from weight loss measurements by using a "spinner" test assembly. The corrosion rate of copper decreased with increasing P-OHO concentration at concentrations over 0.1 m mol/l in the neutral solutions. Corrosion tests revealed that the maximum inhibition efficiency was 98% at a concentration of 1 m mol/l in the solutions of pH 6.0 to 8.6. The polarization curves indicated that P-OHO was a cathodic inhibitor rather than an anodic one.

Reflection-abosprtion infrared spectra of surface films formed on copper in the NaCl solutions in the presence of P-OHO were identified as cupric-octylhydroxamate. It was concluded that the inhibition action is mainly due to the formation of adherent films of the Cu-octylhydroxamate complex on the surface of copper and/or copper oxide. (English)

Intensity-Following Ellipsometry of Passive Films on Iron

R. Nishimura, K. Kudo and N. Sato
Surface Science **96,** 413 (1980)

Structures of passive films on iron formed by a two-step passivation method in acidic and neutral phosphate solutions were investigated by means of intensity-following ellipsometry combined with a cathodic reduction technique. The passive films thus formed were generally composed of a barrier layer and a deposit layer each with different optical constants. In pH below 5.5 the barrier layer was divided into two, and below pH 2 the outer deposite layer was dissolved away. The total thickness of the film at a constant overpotential increased with the solution pH, but the thickness of the film at a constant overpotential increased with the solution pH, but the thickness of the barrier layer was nearly constant irrespective of the pH. (English)

Differential Composition Profiles of Passive Films on Inconel 600 and Incoloy 800 Alloys

M. Seo and N. Sato

Corrosion-NACE **36**, No. 7, 334 (1980)

A differential method for obtaining the exact composition profiles in depth by use of Auger Electron Spectroscopy (AES) and argon ion sputter etching was applied to the surface analyses of Inconel 600 and Incoloy 800 alloys passivated potentiostatically in deaerated 0.5 M sulfuric acid solution, pH 6.48 borate solution, and 0.1 M sodium hydroxide solution, respectively. The multiple surface layer model was applied to the exact composition profiles in depth, and then the surface excess (Γ_I) of component, chromium, iron, and oxygen, relative to the nickel component was obtained as a function of anodic potential. The values of Γ_{Cr} for both alloys decreased with increasing pH of solution. The values of Γ_O for Incoloy 800 are always larger than those for Inconel 600 over the whole range of passivity, irrespective of solution pH. Furthermore, the relation between surface tension (γ) and surface excess (Γ_O) was derived by assuming that the alloys covered with passive films behave as an oxygen electrode. The decrease in surface tension ($\Delta\gamma$) of the alloys due to the film growth for 1 V change in anodic potential was of the order of $-0.1 \sim -0.2$ N cm^{-1}. (English)

Ellipsometry and Auger Analysis of Chromium Surfaces Passivated in Acidic and Neutral Aqueous Solutions

M. Seo, R. Saito and N. Sato

J. Electrochem. Soc., **127**, No. 9, 1909 (1980)

Ellipsometry and Auger electron spectroscopy (AES) were applied in order to elucidate the state and composition of chromium surfaces in deaerated 0.15 M H_3PO_4 (pH 1.55), 0.15 M NaH_2PO_4 (pH 4.38), and borate (pH 6.48 and 8.42) solutions. The cathodic reduction of chromium at -1.19 V (HESS) for 15 min in 0.15 M NaH_2PO_4 (pH 4.38) solution gives a good reproducible bare surface whose refractive index N_s is 4.35–4.15 i. The refractive index of the passive film formed on chromium for 1 hr at constant potential in the passive region is 1.80-(0.0∼0.20) i, independent of the film thickness. In the case of pH 6.48 and 8.42 solutions the film thickness obtained ellipsometrically is in good agreement with that obtained coulometrically. The thickness (0.3∼2.0 nm) of passive films increases linearly with increasing anodic potential and becomes smaller in the solution of the higher pH. The quantiative Auger analysis reveals that the average composition in depth of the passive film is nearly equal to Cr_2O_3 and that only the uppermost surface is hydrated. (English)

Surface Characterization of Stainless Steels Prepared with Various Surface Treatments

M. Seo and N. Sato

Transaction of the Japan Institute of Metals,
21, No. 12, 805 (1980)

The composition depth-profiles of the surfaces of 304 and 316 stainless steels perpared with a variety of surface treatment have been measured by a simultaneous use of argon ion sputter-etching and Auger electron spectroscopy. Chromium was enriched in the surface oxide films, whereas nickel was enriched at the film/substrate interface. The degree of Cr-enrichment in surface films depended on the surface treatment and increased in the following order; mechanical polishing with emery paper in water < chemical etching in mixed acid of 1%HF+10%HNO_3 < electropolishing in mixed acid of $CH_3COOH+HClO_4$ (20 : 1) < chemical treatment in 10% HNO_3 or chemical passivation in 30% HNO_3. The degree of nickel enrichment at the film/substrate face increased with increasing degree of chromium enrichment in the film. The surface oxide films on 304 stainless steel were always thicker than those on 316 stainless steel, irrespective of the surface treatments. The aging of specimen for one week in dessicator gave rise to decrease in chromium-enrichment and to increase in film thickness. Discussion was made on the relationship between pitting potential and surface composition of stainless steels. (English)

Corrosion as a Probabilistic Phenomenon

T. Shibata

J. Metal Finishing Society of Japan,
31, 336 (1980)

Several probability distributions which are commonly observed in localized corrosion have been reviewed with typical examples. The poisson distribution which is the most important and basic distribution in pitting corrosion is explained at first and it is shown that a deviation from the completely random Poisson distribution due to a mutual interaction of pits can be evaluated by H or D function which had been introduced by Masuko. It is also pointed that the exponential distribution observed for the induction time of pit generation has been successfuly explained by assuming a Poisson type stochastic process operating in pitting corrosion. Extreme value analysis for estimating the maximum pit depth and the failure life analysis of electronic parts such as IC using the Weibull distribution are reviewed. (Japanese)

Auger and XPS Analyses of Anodic Oxide Films on Molybdenum in the Transpassive Region

N. Seo, N. Sato and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
29, No. 6, 281 (1980)

Growth and dissolution of anodic oxide films formed on pure molybdenum in deaerated boric-borate solutions of pH 6.48, 8.42 and 10.43 proceed simultaneously at anodic potentials higher than 0.43 V (HESS). The composition of anodic oxide films formed on molybdenum in the transpassive region was analyzed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) combined with argon ion sputter-etching. The uppermost layer (about 1 nm) of the anodic oxide films consists of hexavalent Mo (VI) ions, O^{2-} and OH^- ions, whereas low valent Mo (V), Mo (IV) and Mo (III) ions and O^{2-} ions exist in the inner layer (20～1000 nm) whose composition is uniform in depth. The average valency of molybdenum in the inner layer increases from +3.4 to +5 as the solution pH increases from 6.48 to 10.43. The ratio of film dissolution current density i_D to film growth current density i_O also increases with increasing pH of solution. It seems that the composition of inner layer is determined by kinetic parameters of film growth and dissolution. (Japanese)

Probability Distribution of Failure Times of Stress Corrosion Cracking of 17Cr-11Ni Stainless Steel

T. Shibata and T. Takeyama

Tetsu to Hagane, **66,** No. 6, 693 (1980)

Probability distribution of failure times of stress corrosion cracking 17 Cr-11 Ni stainlese steel under constant stresses of 5 to 30 Kg/mm^2 in 25%, 35%, and 45% $MgCl_2$ solutions at their boiling temperature has been analysed by using the Weibull probability paper which is widely used in reliability engineering. Probability distribution of failure times was found to be described as single or composite Weibull distributions. The composite distribution consisting of mode 1 and mode 2 distributions is found at the low stress conditions. Mode 1 is observed at the earlier failure time region and its shape parameter is larger than unity, depending on the stress and temperature examined. On the other hand, the shape parameter of mode 2 which is observed in the latter region of failure times shows almost a constant value of unity. The condition which gives the shape parameter of unity is likely to correspond to a chance failure or random occurence of crack initiation, while the shape parameter larger than unity indicates a wearout failure which seems to correspond to crack propagation. Thus, the type of distribution of failure times is likely to connect the failure mode, i. e., crack initiation or propagation. (Japanese)

Corrosion Probability and Stress Corrosion Cracking Probability

T. Shibata

Proc. the 25th Japan National Symposium on Strength,
Fracture and Fatigue, p. 1 (1980)

This review paper has emphasized that scattering of data is inherent in localized corrosion and stress corrosion cracking, so that it could not be avoided to introduce a probabilistic or statistical approach to evaluate the experimental data in a quantitative manner. The important contribution by vans to establish the concept of "Corrosion Probability" and the recent development of the stochastic theory of pitting corrosion has been reviewed. Also several works on the analysis of stress corrosion cracking failure time obeying the log-normal or the Weibull probability distribution are shown to indicate the usefulness of the probability concept for evaluating the reliability of materials against corrosion. (Japanese)

H_2S-Catalyzed Hydrogen Absorption in Iron

H. Murayama, M. Sakashita and N. Sato

Proceedings JIMIS-2, "hydrogen in Metals", p. 297
Japan Inst. Metals, Sendai (1980)

Hydrogen absorption in iron in the presence of H_2S was studied using an electrochemical hydrogen permeation membrane cell in weakly acidic acetate solutions. The selectivity factor for adsorbed hydrogen entering into the metal or forming hydrogen molecules was determined as function of electrode potential and H_2S concentration. It appears that the electrochemical combination route $H_{ad}+H^{+}+e\rightarrow H_2$ predominates over the chemical combination. The adsorption of H_2S gives rise to the formation of $(FeS)_{ad}$, which will constitute the catalytic site for hydrogen absorption. (English)

High-Temperature Sulfidation of Fe-Mn Alloys

K. Nishida T. Narita, T. Tani
and G. Sasaki

Oxidation of Metals. Vol 14, No. 1, p. 65 (1980)

The complete range of binary Fe–Mn alloys were sulfidized in pure sulfur vapor (1 atm) at 700–1000°C. It was found that the corrosion kinetics could be divided into four groups, depending upon the alloy concentration. The first group, up to 11 w/o Mn, had a constant corrosion rate. The second group, up to about 63 w/o Mn, had an exponentially decreasing rate of corrosion with increasing manganese content. In the third group, about 63–80 w/o Mn alloys, the corrosion rate did not follow the parabolic law. The corrosion rates became constant above 80 w/o Mn. These corrosin kinetics were explained by considering the scale structure and alloy substrate. (English)

High-Temperature Sulphidation of Some Fe-Mn Alloys Under Low Sulphur Pressures

K. Nishida and K. Godlewski

Proceedings of 9th International Symposium on
Reactivity of Solids, p. 170 (1980)

Three different Fe-Mn alloys (11, 29, and 48 w/o Mn) were sulphided in a H_2-H_2S gas mixture ($Ps_2=10\sim10^{-3}$ Pa) at 973~1273 K. Corrosion kinetics and scale morphologies for these alloys were discussed by using obtained data. (English)

Calorizing of Ta Sheets and Their Oxidation Behavior

K. Nishida and M. Hachinohe

Proceedings of Interfinish 80, p. 377 (1980)

To improve the oxidation resistance of Ta sheets, they were calorized in a quartz ampoule at 1000°C by using Al vapor generated from the powdered $FeAl_2$ alloy. Their oxidation behavior was examined in flowing air (1 liter/min) over the temperature range from 900 to 1300°C. For the best oxidation resistance at 1000°C, the pre-oxidization treatment at 1100°C for a short time (1 hr) was found the most effective for long usage. (English)

Surface Coating of Ta Sheets for Improvement of Oxidation Resistance

K. Nishida and M. Hachinohe

Bulletin of the Faculty of Engineering,
Hokkaido University, No. 98 (1980)

The present paper is to report the results for a long term oxidation at 1100°C and the improvement of the oxidation resistance of the calorized Ta sheets at 900°C and 1000°C (50～55 hr), based on the findings obtained from the previous short term oxidation.

1) The oxidation behavior obtained at 1100°C for 55 hr was similar to that obtained at 1200°C for 5 hr.

2) After the pre-oxidization treatment of the sheet calorized at 1100°C for 1 hr, the sheet was further oxidized at 900°C and 1000°C for 50 hr. As a result, the oxide formed on the sheet was maintained at about 3.3 μm thickness and there was no significant change in the oxide. The original $TaAl_3$ alloy layer was much less decomposed than that oxidized at 1100°C for 55 hr and had no formation of voids. Therefore, for the protection of the calorized Ta sheets against a long term oxidation the short pre-oxidization treatment at 1100°C can be significantly effective. (Japanese)

On the Diffusion of Ternary Electrodeposited Layers of Fe-Ni-Cr and Fe-Cr-Ni

K. Okada and K. Nishida

Tetsu-to-Hagane, 66, No. 9, p. 67 (1980)

The study of diffusion coating on iron has been carried out. The object of this study is how the surface layer of iron can be converted into an Fe-Ni-Cr alloy such as austenitic stainless steel.

The diffusion process chosen for this experiment was solid state process, which was carried out by preparation of ternary metal layers by means of electrodeposition in an order nickel-chromium or chromium-nickel on substrate, followed by heat treatment in the temperature range from 600°C to 1000°C. In the previous paper, data on the diffusion couples consisting of Fe-Cr, Fe-Ni or Cr-Ni, were given. On the basis of these information and thickness of the interface layer in the ternary layers, the time to associate together three elements and the thickness of the diffusion layers consisting of the three elements were presumed.

The time to associate was in accord with that assumed, but the thickness of the diffusion layers were greater than the expected value. The thickness and composition of the diffusion layers were determined by optical microscopy and electron probe micro analysis. One of the reasons that the latter results were shown is considered that nickel dissolving iron or chromium has penetrated rapidly into grainboundaries. (Japanese)

Computor Simulation of Cation Distribution in Solid Solution Scales Formed on Binary Alloys

T. Narita and K. Nishida

Bulletin of Japan Institute of Metals, 19,
No. 12, 874 (1980)

In 1969, Wagner first suggested an analytical calculation for the cation concentrations in a solid solution oxide scale by assuming a constant ratio of cation diffusivities through the scale supporting an oxygen activity gradient.

Dalvi and Coates (1971) performed the first test of Wagner's theory to the actual oxidation of a 10% Ni-Co alloy, calculating the solute cation distribution in the scale by use of the relations between parameters in the applicable differential equations. The calculated results seemed in good agreement with the measured values, but many assumptions were involved in their analysis.

Narita and Nishida (1974) calculated a D_{Ni} value in (Ni, Co) O from $p=(D_{Co}/D_{Ni})$, using D_{Co} (Crow, 1969), and also many D's for solute cations in Fe-base sulfide scales (1975), although such a treatment seems the reverse as compared to the normal process.

Mayer and Smeltzer (1976) could calculate Fe distributions in Co-Fe oxide scales and showed good agreement between calculated and measured values using the variable p's of Crow (1970).

Bastow, Whittle and Wood continued an examination of the influence of parameters appearing in the analytical solution for the cation concentration and they suggested the theoretical results and also an excellent estimate for the rate constant (Kest) (1977). Quite recently Smeltzer and Narita could obtain a more accurate solution for the previous Co-Fe oxide scales by a self-consistent calculation. (Japanese)

Interdiffusion in the ζ-Solid Solution of a Ni-Al System

T. Yamamoto, T. Takashima and K. Nishida

Transactions of the Japan Institute of
Metals, 21, No. 9, 601 (1980)

For the purpose of studying interdiffusion in the ζ-solid solution of a Ni-Al system, the experiments were performed using method of vapor-solid couple at 1273～1573 K. As a vapor source, the fine chips of 12 mass% Al-Ni alloy ($\zeta+\varepsilon$ phases) were used. The surface concentration of Al in the diffusion annealed test pieces almost coincided with the solubility limit reported in the phase diagram of the Ni-Al system at each experimental temperature.

Fine alumina markers placed on the surface of test pieces prior to diffusion were found in its inside after annealing at each temperature. The composition at the marker position indicated a higher Al concentration with an increase in annealing temperature. The ratio of the intrinsic diffusion coefficients of these two constituents, $D_{\mathrm{Al}}/D_{\mathrm{Ni}}$, was 1.3～7.0 at the marker position.

The interdiffusion coefficients ($\tilde{D}$) were dependent upon the annealing temperature and Al concentration, and were evaluated to be the orders of 10^{-15}～$10^{-13}\,\mathrm{m^2/s}$ in this experimental temperature range. Log $\tilde{D}$ increased almost linearly with increasing Al concentration.

The activation energies for interdiffusion ($\tilde{Q}$) obtained from the temperature dependence of $\tilde{D}$ decreased from 282 to 258 kJ/mol with increasing Al concentration. The impurity diffusion coefficeint of Al in Ni, D^{*}_{Al}, at each temperature was obtained from extrapolating of $\tilde{D}$ to 0 at % Al and its activation energy, Q^{*}_{Al}, obtained from the Arrhenius plot of D^{*}_{Al} was evaluated to be 284 kJ/mol.

The relationship between the entropy term, $\tilde{D}_0$, and $\tilde{Q}$ can be represented by the following equation:

$$\ln(\tilde{D}_0/\mathrm{m^2\cdot s^{-1}}) = 3.1\times10^{-5}(\tilde{Q}/\mathrm{J\cdot mol^{-1}}) - 16.0\,.$$

(English)

XPS Studies on Barrier Oxide Films Formed on Aluminium in Neutral Borate and Phosphate Solutions

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

Proccedings of 10th World Congress on Metal
Finishing, p. 281, The Metal Finishing
Society of Japan, 1980.

Pure Al specimens were anodized in neutral borate and phosphate solutions and the distribution of bound water and electrolyte anions in the formed oxide films were determined, using X-ray photoelectron spectroscopy combined with chemical sectioning of the films in a sulfuric acid solution. Results show that the films contain electrolyte anions in the form of BO_2^- and PO_4^{3-} with concentrations decreasing towards the substrate metal. Al exists as a trivalent ion throughout the oxide, but bound water and PO_4^{3-} are not included in the inner part of the films. The chemical composition of the oxide was established as a function of the distance from the outer surface.

Composition of Barrier Type Oxide Films Anodically Formed on Aluminium in a Neutral Borate Solution

H. Konno, S. Kobayashi, H. Takahashi
and M. Nagayama

Electrochimica Acta, **25**, 1667 (1980)

99.99% Al specimens were anodically oxidized in a boric acid-borate solution (pH=7.4, 20°C) by applying a constant potential of 50 V (*vs. sce*). The oxide films formed were compact and had a thickness of about 76 nm. The distributions of Al (III), O (II), and B (III) ions in the films were determined by X-ray photoelectron spectroscopy and chemical analysis combined with chemical sectioning of the films in a sulfuric acid solution. It was ascertained that the film consists of two parts : the average composition of the outer part is $AlO_{1.36}(OH)_{0.28}(B_2O_3)_{0.07}$, and that of the inner part is $AlO_{1.5}(B_2O_3)_{0.027}$. The outer part is slightly hydrated, and in sulfuric acid solutions it dissolves more rapidly than the inner part. Borate ions are distributed through the films with an average concentration of 5.8 wt% as B_2O_3.

Mössbauer Spectroscopic Determination of Chemical State of Iron in Bauxite

T. Morozumi, M. Otsuka and H. Ohashi

Bulletin of the Faculty of Engineering, Hokkaido
University No. 97, 73 (1980)

The chemical state of iron contained in several kinds of bauxite, which are utilized as a raw material in the aluminum industry in Japan, were investigated by Mössbauer spectroscopy. The main compounds of iron were identified from the results, which showed variations of the Mössbauer absorption spectra with calcination and measuring temperature. Although the absorption intensities of the spectra differed significantly, major species identified were paramagnetic or superparamagnetic α-Fe_2O_3 in all of these bauxite samples. The superparamagnetic α-Fe_2O_3 was found mainly in the gibbsite-type bauxite, but not in the boehmite/gibbsite-type or the boehmite-type bauxite. The Mössbauer absorption spectra of red mud and its calcined products were also given.

X-Ray Photoelectron Spectra of Hexavalent Iron

H. Konno and M. Nagayama

Journal of Electron Spectroscopy and Related
Phenomena, **18**, 341 (1980)

Binding energies of Fe 3*p* and Fe 2*p* electrons for K_2FeO_4 were measured and compared with those for γ-FeOOH, α-Fe_2O_3, and for metallic iron.

Acceleration of the Oxidation of Fe^{2+} Ions by Fe (III)-Oxyhydroxides

H. Tamura, S. Kawamura and M. Nagayama

Corrosion Science, **20,** 963 (1980)

Fe^{2+} ions were oxidized by air in neutral solutions containing Fe (III)-oxyhydroxide in the forms of Fe (OH_3) (amorphous), α-FeOOH, β-FeOOH, and γ-FeOOH. This reaction was found to be accelerated by all of the Fe (III)-oxyhydroxides, according to the rate equation :

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

Here, $[Fe^{2+}]_T$ is the sum of the concentrations of free Fe^{2+} and adsorbed Fe^{2+} on Fe (III) (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′ decreased in the order of $Fe(OH)_3 > \alpha$-FeOOH $> \gamma$-FeOOH $> \beta$-FeOOH. The catalytic activity of $Fe(OH)_3$ depends strongly on the manner in which it is prepared. It is shown that k′ is equal to the product of the equilibrium constant for the adsorption of Fe^{2+} (K) and the specific constant for the xoidation of adsorbed Fe^{2+} (k_s). The values for K and k_s have been determined as functions of pH and $[O_2]$ for each Fe (III) species, and the factors determining k_s and K are discussed.

Effects of Neutron and Electron Irradiation on Low-manganese Steels

T. Takeyama, S. Ohnuki and H. Takahashi

Tetsu to Hagane, **66,** No. 1, 122 (1980)

The interaction between solute atoms and defects was studied by means of tensile test and transmission electron microscopy. The defects were produced by neutron irradiation at 200°C to a fluence of 6.4×10^{18} n/cm^2 ($E_n > 1$ MeV) and electron irradiation at 650 kV electron microscope to a fluence of 7×10^{21} e/cm^2.

Radiation hardening and radiation embrittlement occured by neutron irradiation. The yield stress increased and the total elongation decreased with the increase of manganese content. Dislocation loops were observed on iron, but they were not detected on manganese alloys. Therefore, it will be considered that the defects would be trapped by manganese atoms and then formed complex with carbon atoms. On electron irradiation defects were not observed also on the manganese alloys, however the defect clusters, presumably interstitial type, appeared above 325°C and grew during post-irradiation annealing. The annealing behavior was similar for the neutron and electron irradiated specimens.

The radiation hardening could be explained as that manganese atoms trap carbon atoms and interstitial atoms during irradiation and then form fine complexes, which would act as the obstacles for dislocation motion. (Japanese)

The Effect of Precipitation on Void Formation in Copper-Iron Alloy During Electron Irradiation

T. Takeyama, S. Ohnuki and H. Takahashi

Journal of Nuclear Materials 89
(1980) 253-262

Cu–1.5 wt% Fe alloys have been irradiated in a high-voltage electron microscope to study the effect of precipitates on void formation. Voids were formed near the coherent and semi-coherent precipitates and increased in size as the dose increased. These phenomena suggest that the self-interstitial was attracted preferentially to the stress field of the precipitate and consumed to form a dislocation loop, and then a supersaturation of vacancies was produced near the precipitate. In the case of a incoherent precipitate, voids were observed not only near the precipitate but also at dislocations. The results show that void formation in the specimen was mainly affected by the dislocation on the precipitate and in the matrix. Radiation-induced precipitates were formed near the foil surface in the as-quenched specimen. This void formation depended on the change of solute concentration in solution because of the radiation induced solute segregation. The void swelling decreased in order pure Cu, aged Cu–Fe alloys and an as-quenched alloy. (English)

Direct Observation of Radiation Induced Segregation near Grain Boundary and Void in Copper Alloys

T. Takeyama, S. Ohnuki and H. Takahashi

Scripta Metallurgica, Vol. 14, 1105 (1980)

Radiation induced segregation on Cu-2at%Fe and Cu-2at%Ag alloys has been studied by means of an energy dispersive X-ray microanalyzer (EDX) attached to a 200 kV STEM. Electron irradiation has been carried out in a 650 kV high-voltage electron microscope up to 10 dpa at 420∼570 K. Iron which is an undersized solute in copper segregated to grain boundaries and voids which are effective sink site for irradiation produced point defects, and then silver which is an oversized solute depleted to them. The result indicates the direct evidence of the interaction between point defect and solute atom and of the size effect. Moreover, it suggests that the segregation and depletion of solutes affect the nucleation and growth of voids in changing of the defect flow to voids. (English)

The Effect of Temperature on Deformation Structures in Fe–Mn–Cr Austenitic Steel

H. Takahashi, T. Takeyama and T. Hasegawa

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 96, 73 (1979)

The influence of temperature on the deformation structures of Fe–Mn–Cr austenitic steel was studied by means of tensile testing and transmission electron microscopy (TEM) in a temperature range from −70 to 360°C.

Yield stress indicated the temperature dependence below 200°C and the dynamical strain aging occurred between 200 and 300°C at which temperatures the higher work hardening was obtained.

Deformation structure also varied with the temperature and ε-phase was formed at −70°C. With increasing in deformation temperature the yield stress decreased and stacking faults and further dislocations occurred. The stacking fault energies were determined by "in situ experiments" using TEM and it was clarified that the stacking fault energy increases with the increasing in temperature.

Thus, the yield stress and the work hardening were affected by the structures which depend on deformation temperature and stacking fault energy. Furthermore, it seems that the increase in stacking fault energy at higher temperatures would cause mobile dislocations to increase and to interact with carbon atoms in solution during deformation. (Japanese)

Mechanical Properties of Sintered Iron Sheets Containing Reduced Iron Powder with Gangue

Y. Suzuki, S. Sayama and K. Nishida

Transactions of the Iron and Steel Institute
of Japan 21, No. 1, 32 (1980)

Sintered iron sheets containing gangue minerals were produced from iron powder reduced by means of fluidized bed. Effect of gangue from iron ore on the mechanical properties of sintered iron sheets was examined using various oxides. Reduced iron powder was carefully mixed with pure iron powder up to 50 wt%. The mixed powder after pressing was sintered in hydrogen at 850°C or 900°C for 1 hr, rolled and annealed at 700°C or 850°C for 1 hr. Then, the effect of gangue oxides dispersed in the sintered iron sheets on the mechanical properties was examined. As the content of oxides in the sheets increased, the yield stress and tensile strength increased, while the elongation decreased. After a high temperature annealing in hydrogen, the elongation improved because of a decrease in the oxygen content of sheet, while the strength decreased owing to reduction of oxides during heat treatment.

The oxides changed into glassy ones during reduction. Oxide layers were found in parallel to the rolled surface of iron sheet. The oxides contained in sintered iron sheets are effective to increase the tensile strength of sheets when they are treated at comparatively low temperatures (700°C or 850°C). It seems to be due to the formation of fine oxide particles in the matrix by rolling. (English)

Mechanical Properties of Sintered Iron Sheets Containing Reduced Iron Powder with Gangue

Y. Suzuki, S. Sayama and K. Nishida

Tetsu-to-Hagane, 66, No. 3 66 (1980)

In order estimate the possibility of utilization of reduced iron powder produced by a fluidized bed, an examination was made on the effect of gangue minerals in iron ore on the mechanical properties of sintered iron sheets which contained various oxides of the gangue. Reduced iron powder was carefully mixed with pure iron powder up to 50%. The mixed powder was sintered at 850°C or 900°C for 1 hr in hydrogen after pressing, and then rolled and annealed.

The effect of gangue oxides dispersed in the sintered iron sheets on the mechanical properties was examined. As the content of oxides in the sheets increased, the yield stress and tensile strength increased, but the elongation decreased. After a high temperature annealing in hydrogen, its elongation was improved because of the decrease of oxygen content in iron sheets, while the strength decreased owing to the reduction of oxides during heat treatment in hydrogen.

These oxides of gangue minerals in iron ore changed into glassy ones during reduction. The oxide layers were found to be parallel to the rolling face in iron sheet. These gangues contained in the sintered iron sheet are effective to increase the tensile strength of the sheets produced at lower temperatures. This is seemed to come from the reason that these oxides are crushed and become to be fine particles in the matrix during the rolling. (Japanese)

Mechanical Properties of Sintered Iron Sheets Containing Dispersed Oxide Particles

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

Transactions of The Iron and Steel Institute
of Japan, 20, 422 (1980)

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

The effects of fine oxide particles (amorphous SiO_2 and γ-Al_2O_3: about 200 Åϕ) on the mechanical properties of the sheet were found to be remarkably high as compared with those of larger size (α-SiO_2 and α-Al_2O_3: about 2 μmϕ). With fine oxide particles the elongation decreased generally owing to the fine recrystallized grain size in the matrix, though an increase appeared in the range of $0.4 \sim 0.7$ vol% additions. This fact suggests that the elongation is affected by the annealing texture which has been changed by the added oxide.

As a result, it was found that the dispersed oxide particles and the restraint on the recrystallization of the sheet by these particles increased 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. (English)

Ruture Strength of Cast Iron Bar with Circumferential Notch

T. Noguchi

Journal of the Society of Materials Science
29, No. 319, 387 (1980)

In order to clarify the reason of low notch sensitivity in the strength of cast iron, tensile tests and stress analyses were performed on the circumferentally notched bars of flake and nodular cast iron. A fracture criterion was induced from the non-elastic stress distributions obtained by FEM.

The experiments showed that the rupture load of flake cast iron was varied only by ±5% at room temperature by the notches with the elastic stress concentration factor up to 2. 6. Accordingly the flake cast iron showed very low notch sensitivity. The stress analyses revealed that such low sensitivity was caused by the release of stress concentration due to the non-elastic behavior and the existence of the stress boundary layer δ of 2~3 mm in depth. At liquid nitrogen temperature the iron showed high notch sensitivity because of its highly elastic behavior and the decrease in δ.

For the nodular cast iron, the rupture load of notched bars was increased by 15~25%. This increase in strength was attributed to the constraint of deformation and fracture at the notch root. (Japanese)

Finite Element Method Analysis of Bending Strength of Cast Iron Circular Plates

T. Noguchi and K. Nagaoka

IMONO, 52, (2), 94 (1980)

In order to understand why high bending strength can be induced in cast iron plates, bending test and the non-elastic stress analysis by FEM were performed on circular plates under distributed load. Though the theories used in the program did not completely describe the elasto-plastic behavior of cast iron and the analysis on bending plates was only approximate, calculation of stress distribution revealed the following. Due to the nonelastic behavior of cast iron, the maximum bending stress in the plate at the fracture load was about 60% of the elastically calculated value. Maximum stress exceeded the tensile strength of the material by 20～70%, and several cracks were observed on the tensile surface of the plate before the maximum load. Final fracture occured at the load which was 1.2～1.8 times that of calculated load where the bending stress reached the tensile strength. This was attributed to the stress distribution in the plate. Accordingly the ratio of conventional bending strength to the tensile strength was calculated to be 2.0～3.0 using the elastic formula, that is just the same as obtained experimentally in the paper presented before this one. It is suggested that the ratio is high in low strength iron and also changes depending on the thickness of the plate. (Japanese)

Falling of 50T JiB-Crane in Hakodate-Dock Shipyard

K. Nagaoka and T. Noguchi

Journal of Japan Society for Safety Engineering
19, No. 1, 40 (1980)

Failure analysis was applied to investigate the cause of an accident occurred by falling of a giant jib-crane 50 T at Hakodate-Dock shipyard being in construction. As the results of collation of feature of fracture and mechanical condition of many failed parts it was induced that the prime failure might be buckling of center post or leg of roller path. Finally mechanical failure analysis gave the conclusion that thin plate of center post buckled initially and then the post yielded at the corner before the falling of the crane.

According to a consideration on the design, the condition of failure and the procedure of construction, the center post might be buckled elastically in service, though the crane had constructed safely by another way. Therefore the accident was caused by a deficiency in design of the center post about the buckling of thin plate sturctures. (Japanese)

Recovery of Hydrogen from Hydrogen Sulfide with Metals or Metal Sulfides

H. Kiuchi, I. Nakamura, K. Funaki
and T. Tanaka

Proceedings of the 3rd World Hydrogen Energy
Conference, Vol. 1, P. 401-411 (1980)

The following two types of reactions were investigated for the recovery of hydrogen from hydrogen sulfide:

Type 1 $H_2S=H_2+S^\circ$, Type 2 $H_2S+O_2=SO_2+H_2$

Each type of reaction is constructured by two-step cycle, in which H_2S is reacted with metal or metal sulfide and then the resulting sulfide undergoes thermal decomposition or oxidation. Ag, FeS, Co_9S_8, Ni_3S_2, and double sulfide such as $CuFeS_2$ were examined in the former type of reaction, while Ag, Cu, Ni, liquid Pb, and liquid Bi-Ag alloy were used as an intermediate in the later. (English)

Mutual Reaction of Lead Sulfide with Lead Sulfate

H. Kiuchi, I. Nakamura and T. Tanaka

Journal of the Mining and Matallurgical Institute
of Japan, 96, 417 (1980)

Recently, the roast-reaction in lead sulfide has been expected to come to the fore in relation to the days of high grade lead concentrates and energy conservation. In addition, the roast-reaction is noteworthy in the following thermochemical splitting of hydrogen sulfide:

$$\begin{array}{c} 2Pb(1)+2H_2S=2PbS+2H_2 \\ PbS+2SO_2=PbSO_4+2S^0 \\ \underline{PbS+PbSO_4=2Pb+2SO_2} \\ 2H_2S=2H_2+2S^0 \end{array}$$

Experiments were carried out by using mixtures of galena powder and reagent grade $PbSO_4$ over the temperature range 650 to 750°C in a stream of inert gas. The progress of the reaction was followed with continuous analysis of evolved SO_2. The reaction products were analyzed by X-ray diffraction.

From the results obtained in this study, it can be concluded that:

1) It has been demonstrated that gaseous PbS was thought to take an important part in the Pb formation.

2) $PbSO_4$ is rapidly converted into $PbO \cdot PbSO_4$ in the presence of gaseous PbS.

3) This basic sulfate changes from $2PbO \cdot PbSO_4$ to $4PbO \cdot PbSO_4$.

4) Over the lower temperature range, $4PbO \cdot PbSO_4$ is easy to produce metallic lead by the reaction with gaseous PbS.

5) Increasing temperature tends to promote the formation of metallic lead form $2PbO \cdot PbSO_4$.

These conclusions could be supported thermodynamically by $\log P_{SO_2} - \log P_{PbS(g)}$ equilibrium diagram. (Japanese)

The Rate of Sublimation of Lead Sulfide

H. Kiuchi and T. Tanaka

Journal of the Mining and Metallurgical
Institute of Japan, 96, 483 (1980)

Using a thin disk made of the powder of galena single crystals from several mines or synthetic lead sulfide, the sublimation rate of lead sulfide has been measured thermogravimetrically at atmospheric and reduced pressures in a stream of inert gas. The limiting gas velocity for the rate of sublimation respectively appeared as the velocity was elevated.

The apparent activation energy for the sublimation was found to be independent of pressure and was determined to be about 54 kcal/mol. This value is nearly equal to the enthalpy of sublimation of lead sulfide.

The experimental results indicated that the sublimation rate was controlled by diffusion of gaseous lead sulfide through the gas boundary layer.

The rate of sublimation under argon was nearly equal to that under nitrogen, but was only half the rate under helium. Decrease in the sublimation with increasing pressure of inert gas was also observed. These two results can be rationalized as reflecting the change in diffusion coefficient of inert gas.

Decrease in the sublimation area may be expected by mixing lead sulfide with a nonvolatile substance or by changing grain size of the lead sulfide particles in a disk. Therefore, a disk containing 13 wt-% alumina was tested. The rate curve showed good agreement with that obtained from the specimen of pure lead sulfide in the incipient sublimation. Moreover, it was found that grain size of lead sulfide particles in a disk had no effect upon the sublimation rate. It may, therefore, be concuded that the section area for diffusion of gaseous lead sulfide correspond to the area, not of the lead sulfide on the disk, but of the surface of the disk. (Japanese)

Use of Hydrogen Sulfide as a Source of Hydrogen

H. Kiuchi, K. Funaki and T. Tanaka

Proceedings of 4th Joind Meeting MMIJ-AIME,
E-2-5, P. 67-82 (1980)

In this research, the two-stage thermochemical cycle was proposed as described below and experimental studies were made on the cycle.

$$\begin{array}{l} Ni_3S_2 + H_2S = 3NiS + H_2 \\ 3NiS = Ni_3S_2 + S \\ \hline H_2S = H_2 + S \end{array}$$

In the case where Ni_3S_2 alone was used, the sample was sintered or partly fused due to to the fusion point depression resulting from the change in composition on the thermal decomposition of formed NiS. Countermeasures taken against the problems could prevent the nickel sulfide particles, which were mixed and dispersed in inert powder, such as Al_2O_3 or MoS_2, from sintering. Thus, the cyclic reactions were permitted to provide a stationary high decomposition of H_2S.

The utilization of polysulfide, such as MS_2, has so far bcen taken up in this kind of cycle. This research showed that the use of lower sulfides such as Ni_3S_2 was regarded as rather important based on the thermodynamic investigation of the respective reactions consisting the cycle. The comparison between the sulfurization reactions of NiS to NiS_2 and of Ni_3S_2 to NiS further showed that the latter was superior to the former in kinetics and H_2 concentration. (English)

Studies on the Pyrohydrolysis of Metal Chlorides. I. The Pyrohydrolysis of $NiCl_2$, $CoCl_2$, and $FeCl_2$

R. Shibayama, N. Tsuchida and T. Tanaka

Denki Kagaku 48, 545 (1980)

Pyrohydrolysis of $NiCl_2$, $CoCl_2$, and $FeCl_2$ were investigated in the temperature range 450 to 700°C. It was found that NiO and CoO were formed respectively as a solid product during pyrohydrolysis of $NiCl_2$ and $CoCl_2$ and that experimental values of the conversion ratios of steam into HCl(g) agreed well with the thermodynamic predicition. However, in the pyrohydrolysis of $FeCl_2$, the temperature dependence of experimental values for the conversion ratio differed significantly from the calculated based on the following one-stage reaction $3FeCl_2+4H_2O \rightleftarrows Fe_3O_4+6HCl+H_2$. The reaction mechanism shown below was suggested, in which gaseous FeO was formed as a transient intermediate.

$$FeCl_2+H_2O \longrightarrow FeO+2HCl$$
$$3FeO+H_2O \longrightarrow Fe_3O_4+H_2$$

It was also concluded from the observation of crystal growth of metal oxides that vapors of metal chlorides participated virtually in the reaction of the pyrohydrolysis. (English)