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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. Y. Otake,  
Mr. N. Kameda and Mrs. H. Akatsuka

***Students***

M. Koda, K. Ebihara, Y. Horii, K. Sato, M. Mukai,  
N. Fujimoto, T. Hirose and N. Ogane

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 returned to the group from Clarkson College, Potsdam, N. Y., U. S. A., in August. Dr. Konno left in the same month to work with Prof. H. Leidheiser, Jr. at Lehigh University, Bethlehem, P. A., U. S. A.

Main subjects 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  $\text{PO}_4^{3-}$  and  $\text{OH}^-$  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 sulfuric acid to examine the morphology and the density of the films using electron microscopy, gravimetry 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

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water.

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

(4) Air-oxidation of  $\text{Fe}^{2+}$  ions in near neutral solutions.

Ferrous ions can be oxidized by air to form Fe(III)-oxyhydroxides in aqueous solutions. The rate of reaction is accelerated by the reaction product as well as the coexisting cations ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ) and anions ( $\text{HPO}_4^{2-}$ ,  $\text{F}^-$ ). Some anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) retard the reaction. The combined effect of Fe-oxyhydroxides and the particular anions or cations on the kinetics of the oxidation of  $\text{Fe}^{2+}$  ions are being examined.

(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  $\text{O}_2$  and anions using mainly XPS. It was found that a mono molecular layer of phosphate and chromate ions are adsorbed to prevent the film from 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.

(7) Adsorption of cations and anions on the surface of Fe(III)-oxyhydroxides.

The amount of cations ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) adsorbed by Fe(III)-oxyhydroxides are measured as functions of the solution pH and the concentrations of the adsorbates. Attempts are being made to explain the adsorption behavior in terms of surface complexation.

## Oral Presentation

Inhibitive Effects of Chromate and Phosphate Ions on the Hydration of Barrier Type Anodic Oxide Films on Al; S. Kobayashi, H. Konno and M. Nagayama : The 7th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1981.



pH Effect on the Chemical Structure of Anodic Oxide Films Formed on Al in Phosphate Solutions; K. Fujimoto, H. Takahashi, H. Konno and M. Nagayama: *Ibid.*, Jan. 1981.

Impedance Study on the Hydration of Porous Anodic Oxide Films on Al with Hot Water; M. Koda, H. Takahashi and M. Nagayama: The 16th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1981.

Effect of Anodizing Condition on the Physicochemical Properties of Porous Anodic Oxide Films on Al; K. Ebihara, H. Takahashi and M. Nagayama: The 1981 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Chem. Soc. Japan, Feb. 1981.

Inhibition of Deterioration of Oxide Films on Al in Solutions Containing Chromate and Phosphate Ions; S. Kobayashi, H. Konno and M. Nagayama: The 63rd Meeting of the Metal Finishing Soc. Japan, Mar. 1981.

Impedance Change of Anodic Oxide Films on Al during Hot Water Treatment; M. Koda, H. Takahashi and M. Nagayama: *Ibid.*, Mar. 1981.

Structure and Properties of Porous Anodic Oxide Films Formed on Al at Different Anodizing Condition; K. Ebihara, H. Takahashi and M. Nagayama: *Ibid.*, Mar. 1981.

pH Effect on the Anodizing Behavior of Aluminum in Phosphate Solutions; H. Takahashi, K. Fujimoto and M. Nagayama: *Ibid.*, Mar. 1981.

XPS Studies of  $\left[ (\text{NH}_3)_4\text{Co} \left\langle \begin{array}{l} \text{O} \\ \text{O} \end{array} \right. \text{C} \begin{array}{l} \text{O} \\ \text{NO}_2 \end{array} \right\rangle \right]^{n+}$  ( $n: 2.1$ ) and  $\left[ \text{en}_2\text{Co} \left\langle \begin{array}{l} \text{NH}_2 \\ \text{O}_2 \end{array} \right. \text{Coen}_2 \right]^{n+}$  ( $n: 4.3$ ); Y. Yamamoto, M. Mori and H. Konno: The 43rd Spring Meeting of the Chem. Soc. Japan, Apr. 1981.

Synthesis of  $(\text{NH}_3)_4\text{Co} \left\langle \begin{array}{l} \text{O} \\ \text{O} \end{array} \right. \text{C} \begin{array}{l} \text{O} \\ \text{NO} \end{array} \right\rangle \text{Cl}_2 \cdot \text{H}_2\text{O} \cdot \text{HCl}$  and its pro-

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- perties; Y. Yamamoto, H. Kudo, M. Mori and H. Konno: *Ibid.*, Apr. 1981.
- Change in the Acid Dissolution Characteristics of Anodic Oxide Films on Al with Hot Water Treatment; M. Koda, H. Takahashi and M. Nagayama: The 1981 Summer Meeting of the Hokkaido Sections of Chem. Soc. Japan and the Japan Soc. for Anal. Chem., Jul. 1981.
- Effects of Phosphate Ions and Fe(III)-phosphate Colloid on the Air Oxidation of  $\text{Fe}^{2+}$  Ions in Aqueous Solutions; K. Sato, H. Takahashi, H. Tamura and M. Nagayama: *Ibid.*, Jul. 1981.
- Aquatic Chemistry and Corrosion; M. Nagayama: Symposium on the solution chemistry of local corrosion sponsored by Japan Institute of Metals, Jul. 1981.
- Corrosion Products of Fe Exposed to Hot Water; H. Konno: Seminar of the corrosion of metals in high temperature water sponsored by the Hokkaido Corrosion Research Association, Aug. 1981.
- Colloid Chemical Studies of Corrosion at Clarkson College; H. Tamura: Seminar of water chemistry sponsored by IRI, Aug. 1981.
- ESCA Studies on the Corroded Surface of Carbon Steel; M. Nagayama: *Ibid.*, Aug. 1981.

## HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

Prof. Dr. K. Nishida, Assist. Prof. K. Atarashiya  
Dr. T. Narita, Mr. K. Sugawara  
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T. Shimawaki, Y. Nagase and K. Taue

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. A new research program was commenced for the ceramic-metal bonding. The research subjects in progress are as follows :

(1) Sulfidation: Sulfidation of SUS316L stainless steel and some Fe-Ni alloys were investigated by using of TGM, X-RAY, EPMA and the newly installed SEM-EDAX system to reveal the effect of alloying elements of Cr and Ni on the internal and/or grain boundary sulfidation. Sulfidation of pure Cr-metal and the high-carbon Cr steels is at present being investigated.

(2) Oxidation: Computer simulation of Co-Ni and Co-Fe alloy oxidation at high temperatures was completed and the extension of the computer program is now in progress from the single oxide scale to the duplex one.

(3) Corrosion in SO<sub>2</sub> gas atmospheres: The effect of oxygen content on the corrosion of pure iron in Ar-SO<sub>2</sub> gas mixtures was investigated. In contrast to pure iron, pre-oxidation treatment of Fe-Al alloys improved significantly their anticorrosion properties against the SO<sub>2</sub> gas attack.

(4) Surface coating: Characterization of the aluminized Nb- and Ta-metals and their oxidation behaviors were investigated.

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Boron films as one of the first wall candidate materials of the fusion reactor was physical vapor deposited on a SUS316L s. s. and then sputter and irradiation properties of the B-film was tested.

(5) Inter-diffusion studies : As a series of the vapor-solid diffusion studies Cu-Ni and Co-Zn binary alloys were investigated. Inter-diffusion between  $\text{Cr}_2\text{O}_3$  powder and the poly- or single-crystals of  $\text{Al}_2\text{O}_3$  were determined and reliable data were obtained for the single crystal of  $\text{Al}_2\text{O}_3$ .

(6) Ceramic-metal bonding : Bonding experiment between  $\text{Al}_2\text{O}_3$  and Ni-metal with Cu-O alloys as a filler revealed that bonding strength was dependent upon the oxygen content in the Cu-O alloy and bonding temperatures.

### Oral Presentation

Coating of the Low-Z Materials by the D. C. Assisted Glow Discharge ; T. Narita, K. Nishida and T. Takeyama : The 16th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 1981.

The Oxidation of Binary Alloys to Form Solid Solution Scales ; K. Nishida : International Conference on High Temperature Corrosion (Sandiego, U. S. A.), Mar. 1981.

Corrosion Behavior of Fe-Mn Alloys at 1073 K in Ar-SO<sub>2</sub> Gas Atmospheres ; K. Kurokawa, T. Narita and K. Nishida : The Spring Meeting of the Japan Institute of Metals, April, 1981.

Intrinsic Diffusivities of the alpha-Solid Solution in the Cu-Zn Binary System by The Vapor-Solid Diffusion Method ; T. Yamamoto, T. Takashima and K. Nishida : *ibid.*, April 1981.

High-Temperature Sulfidation of Some Fe-Ni alloys in H<sub>2</sub>-H<sub>2</sub>S Atmospheres ; K. Kitajima, T. Narita and K. Nishida : *ibid.*, April, 1981.

The Influence of Oxide gangues on the High-Temperature Strength and Fatigue Strength of the Sintered Iron Sheets ; Y. Suzuki, T. Tsurue and K. Nishida : The Spring Meeting of Iron and Steel Institute of Japan, April, 1981.

High-Temperature Corrosion of Pure Iron under Low SO<sub>2</sub> Pressures

- Scale Structures and Mechanism of the Sulfide Formation—; K. Kurokawa, T. Narita and K. Nishida: The Hokkaido Section Meeting of JIM, June, 1981.
- Computer Simulation of the Cation Profiles in the Sulfide Scales Formed on Fe-Ni Alloys; K. Kitajima, T. Narita and K. Nishida: *ibid.*, June, 1981
- Sulfidation Behavior of Fe-Cr-Mn Alloys —Sulfidation Kinetic and Scale Morphology—; M. Morikawa, T. Narita and K. Nishida: *ibid.*, June, 1981.
- Inter-Diffusion of a Ni-Cu Alloy System; T. Takashima, T. Yamamoto and K. Nishida: *ibid.*, June, 1981.
- Inter-Diffusion in the  $\beta_2$  Phase of the Fe-Ni-Al ternary Alloy System; T. Yamamoto, T. Takashima and K. Nishida: *ibid.*, June, 1981.
- Corrosion of the Fe-Based Binary Alloys under Low Sulfur Pressures; K. Nishida: The Tokyo Section Meeting of JIM, July, 1981.
- High-Temperature Sulfidation of Fe-Mn Alloys under Low Sulfur Pressures; K. Nishida: Gordon Research Conference (Corrosion) (New London, U. S. A.) July, 1981.
- Morphology of Scales Formed on Some Fe-Mn Alloys under Low Sulfur Pressures at High Temperatures; K. Nishida and T. Narita: 8th International Congress on Metallic Corrosion (Mainz, West Germany), Sep., 1981.
- High Temperature Corrosion of Super Alloys (Fundamental Lecture); K. Nishida: The Fall Meeting of The Japan Institute of Metals, Nov., 1981.
- Observation of the Scale Formed on Iron at High Temperature under Low SO<sub>2</sub> Partial Pressures; K. Kurokawa, T. Narita and K. Nishida: *ibid.*, Nov., 1981.
- Sulfidation Properties of Fe-Cr-Al Ternary Alloys in H<sub>2</sub>S-H<sub>2</sub> Atmospheres at High Temperatures; T. Narita and K. Nishida: *ibid.*, Nov., 1981.
- High Temperature Sulfidation of Metallic Materials; K. Nishida: The 3rd Working Group in NEDO, Tokyo, Nov., 1981.
- The Effect of Gas Composition on the Corrosion Behavior of Pure

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Iron in the O<sub>2</sub>-SO<sub>2</sub> Gas Mixtures; K. Kurokawa, T. Narita and K. Nishida: The Hokkaido Section Fall Meeting of JIM, Nov, 1981.

Mechanical Properties of the Sintered and Rolled Iron Sheet Made from the Reduced Iron Powder; Y. Suzuki and K. Nishida: *ibid.*, Nov., 1981.

Sulfidation Behavior of a SUS 316L Stainless Steel; K. Kitajima, T. Narita and K. Nishida: *ibid.*, Nov., 1981.

**NUCLEAR REACTOR MATERIALS LABORATORY**

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

***Students***

M. Otsuka, T. Suzuki, S. Doi, K. Ogura, N. Sato,  
H. Togashi, M. Nakai, M. Yoshizumi  
and U. Watanabe

Dr. Moriya continues to work with Prof. M. B. Ives at the McMaster University, Hamilton, Ontario, Canada. He will return on this November.

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

(1) Mössbauer absorption spectra of iron, which was oxidized with water vapor of 1 atom. at temperatures from 250 to 300°C, were measured. From absorption spectra, oxidation products were identified and quantitatively determined.  $\text{Fe}_3\text{O}_4$  was identified as a main corrosion product from the Mössbauer absorption spectra. A red-brown product, which was seemed to be  $\alpha\text{-Fe}_2\text{O}_3$ , was also observed visually on the iron surface especially after a long period of oxidation. Kinetic analyses were also carried out.

(2) Investigation of diffusion of hydrogen during electrochemical growth of zirconium hydride layer was continued. Cathodic polarization in deuterated solution for a given period was followed by that in a light water solution under the same condition. Then D/Zr and H/Zr atomic ratios were determined with etching method and gas chromatography. It was found that the deuterium absorbed in the first place was pushed into the interior of specimen by the hydrogen that was absorbed later. The experiments in reverse sequence elucidated the similar effect. Kinetic analysis was carried

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out on the basis of possible mechanisms.

(3) Investigation of deuterium retention in metals bombarded with 100 keV deuteron was continued. Fe, Ni, Mo, Pd, Ti, Zr and W targets were bombarded with deuteron beams from a Cockcroft-Walton accelerator at  $-196$ ,  $-80$  and  $20^\circ\text{C}$ , and changes in neutron counts were measured with a  $\text{BF}_3$  counter. A peculiar phenomenon that the buildup of neutron count was most rapid at  $-196^\circ\text{C}$  was found in some metals. The modelling of retention process were tried on the basis of composed processes of implantation, diffusion and release, but exact explanation of the above phenomenon has not yet obtained.

(4) An application of controlled potential coulometry to determine a small amount of uranium in solution sample was investigated. The procedure of this analysis consists of reduction of  $\text{UO}_2^{2+}$  to  $\text{U}^{4+}$  with  $\text{Fe}^{2+}$  in strong  $\text{H}_3\text{PO}_4$  solution, selective oxidation of excess  $\text{Fe}^{2+}$  with  $\text{HNO}_3$ , and final electrochemical oxidation of  $\text{U}^{4+}$  on the Pt gauze electrode. The current-time curve in the last electrochemical process was obtained by controlled potential coulometry, and the data was analyzed on the basis of the electrode process of  $\text{U}^{4+}$  oxidation, which was delayed by unknown homogeneous reaction in the solution. The amounts of uranium determined by two analytical methods of the current-time curves, integration with analytical equation and graphical integration, were agreed fairly well each other. Apparent first order rate constant of the reaction in solution was determined as a function of several experimental parameters.

(5) The investigation of hydrogen absorption was continued for iron-titanium alloys with nonstoichiometric compositions. Slow initial absorption rate of stoichiometric alloy, FeTi, was much improved by slight shifting the Ti/Fe ratio toward  $\text{FeTi}_{1.1}$  or  $\text{FeTi}_{1.2}$ . The addition of manganese, which much improved the absorption performance of stoichiometric FeTi alloy, was not effective for nonstoichiometric alloys. Metallographic explanation of these observations was given on the basis of SEM studies.



**Oral Presentation**

- Changes in Surface Condition of Titanium Caused by Absorption of Hydrogen; T. Shindo, M. Moriya and T. Morozumi: The 7th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan., 1981.
- Prevention of hydride Formation on Titanium Cathode by Polarization Added Anodic Pulsating Current; T. Shindo and T. Morozumi: The 16th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1981.
- Improvement of Absorption-Desorption Characteristics of Hydrogen of Titanium-Iron Alloys; T. Mizuno, K. Itoki and T. Morozumi: The 1981 Winter Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., Feb., 1981.
- Diffusion Behavior of Absorbed Hydrogen in Zirconium Metal Surface; T. Sato, T. Mizuno and T. Morozumi: *ibid.*, Feb., 1981.
- Mössbauer Recoil Characteristics of  $\text{Fe}_3\text{O}_4$  Formed During High Temperature Oxidation of Iron; H. Ohashi, M. Otsuka, T. Itaya and T. Morozumi: *ibid.*, Feb., 1981.
- Migration of Hydrogen in Hydride Formed on Zirconium Surface by Cathodic Polarization; T. Mizuno, T. Sato and T. Morozumi: The Annual Meeting of Japan Society of Corrosion Engineering, May, 1981.
- Mössbauer Spectroscopic Characteristics of  $\text{Fe}_3\text{O}_4$  Formed During High Temperature Oxidation of Iron; H. Ohashi, M. Otsuka, S. Doi and T. Morozumi: *ibid.*, May, 1981.
- Improvement of Hydrogen Storage Performance and Its Relation to Texture of FeTi Alloys; T. Mizuno and T. Morozumi: The 1981 Summer Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., July, 1981.
- Characterization of  $\text{Fe}_3\text{O}_4$  Formed During Oxidation of Iron and Steel by Measurement of Debye Temperature; H. Ohashi, S. Doi, M. Otsuka and T. Morozumi: *ibid.*, July, 1981.

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- Mössbauer Spectroscopy as a Measure of Corrosion Measurement ;  
T. Morozumi and H. Ohashi: The 44th Autumn Meeting of  
Japan Chem. Soc., Oct., 1981.
- Hydrogen Energy ; T. Morozumi: Muroran District Meeting of  
Hokkaido Section of Japan Chem. Soc., Nov., 1981.
- Hydrogen and Metals ; T. Morozumi: Kushiro District Meeting  
of Hokkaido Section of Japan Chem. Soc., Nov., 1981.
- Hydrogen Energy ; T. Morozumi: Asahikawa District Meeting of  
Hokkaido Section of Japan Chem. Soc., Nov., 1981.

**ELECTROCHEMISTRY LABORATORY**

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

***Research Fellow***

Dr. Chin-Gen Kin (China)

***Students***

Y. Sera, T. Sakon, M. Masuda, K. Azumi, I. Shintani,  
M. Nagao, T. Shimakura, F. Baba,  
S. Ono and T. Nakagawa

Research subjects in this laboratory are concerned with surface oxide films of pure metals and corrosion-resistant alloys. To examine the composition, structure, and electrochemical properties of the films AES, XPS, ellipsometry, spectro-reflectometry, and electrochemistry are being used. Subjects of the Research in progress are as follows.

(1) Surface enrichment and depletion of alloying elements in iron-base alloys during anodic and atmospheric oxidation.

(2) Relation between the electronic properties and the change in compositional structure caused by heat treatment of Ta and Nb electrodes covered with anodic oxides.

(3) In-situ optical measurements of passive films on Ti, Fe, and Ni.

(4) Growth and reduction kinetics of the passive films on a rotating ring-disc Fe electrode accompanying non-stationary dissolution.

(5) Formation of hydrous iron oxide films precipitated on Al-brass electrodes.

(6) Correlation between the ion-selectivity of hydrous oxide precipitate films and the crevice corrosion of metals.

## CURRENT ACTIVITIES

(7) Anion-adsorption in hydrous oxide films on metal electrodes.

(8) Electrochemical characterization of zinc phosphating films on steels.

Prof. Sato attended the 8th Intern. Congr. on Met. Corr. held 6-11 Sept. in Mainz, FRG, to give a plenary lecture on the passivity breakdown and pitting, and the 22nd Corrosion Science Symposium held 15-18 Sept. in Newcastle Upon Tyne, England, with a paper on ellipsometric study of passive films on titanium in phosphate solutions. Afterwards he stayed at the Corrosion and Protection Centre in the University of Manchester Institute of Science and Technology (UMIST) for 6 weeks. He participated in the Electrochemical Society-Ontario-Quebec Section Autumn Symposium held 30 Oct. in Ottawa, Canada, with a paper on localized corrosion of metals. Assist. Prof. Seo also attended the 8th Intern. Congr. on Met. Corr. in Mainz with a paper on titanium enrichment in anodic oxide film on Fe-3%Ti alloy.

Foreign visitors to this laboratory in 1981 are Dr. G. Horányi of the Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Hungary, on 20 June, Prof. M. Froment of Centre National de la Recherche Scientifique, France, on 9-10 July, Dr. E. R. Papeleo of CBMM, Brazil, on 14 July, and Dr. H. Takenouti of Centre National de la Recherche Scientifique, France, on 13-14 Aug.

### Oral Presentation

Recent Progress in Corrosion Science; N. Sato: The 100th Meeting of the Corrosion and Protection Committee in the Soc. of Materials Sci. Japan, Jan. 1981.

Ellipsometry of Anodic Oxide Film on Titanium in Sulphate and Phosphate Solutions; M. Masuda, T. Ohtsuka, and N. Sato: The 7th Hokkaido Section Meeting of the Electrochem. Soc. Japan, Jan. 1981.

Selective Dissolution and Film Composition of Fe-3Ti Alloy; M. Matsumura, M. Seo and N. Sato: The 16th Annual Meeting

- of the Hokkaido Corrosion Research Association, Jan. 1981.
- Depth-Composition Profile of Oxidation Film on Fe-30Ni Alloy ; M. Seo and N. Sato : *ibid.*, Jan. 1981.
- Corrosion Rate Monitoring by Linear Polarization Method —Corrosion Rate of Iron— ; T. Ohtsuka and N. Sato : *ibid.*, Jan. 1981.
- Introduction to Corrosion Protection of Metals ; N. Sato : 1981. Short Corrosion Course in the Hokkaido Corrosion Research Association, Feb. 1981.
- Elektrochemische Reaktion an HgTe und  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  Elektrode ; M. Sakashita : Seminar für elektrochemische Probleme, Berlin, ERG, Feb. 1981.
- Non-stationary Dissolution of Passive Iron in Acidic Phosphate Solution by Means of Ring-Disc Electrode ; T. Ohtsuka, I. Shintani and N. Sato : The 48th Meeting of the Electrochem. Soc. Japan, March 1981.
- Electrochemical Reactivity and Composition of Tantalum Electrode Covered with Heat-Treated anodic Oxide Film ; T. Sakon, M. Seo, T. Ohtsuka and N. Sato : *ibid.*, March 1981.
- Composition Profile in Depth of Passive Film on Fe-3Ti Alloy ; M. Matsumura, M. Seo and N. Sato : The Spring Meeting of the Japan Inst. Met., April, 1981.
- Ion-Selective Precipitate Films of Corrosion Products (Address for 1980 Corrosion Prize) ; Y. Yomura, M. Sakashita and N. Sato : The Annual Meeting of the Japan Soc. Corr. Engineering, May, 1981.
- Measurement of Anodic Oxide Film on Titanium in Phosphate and Sulphate Solutions by Ellipsometry ; T. Ohtsuka, M. Masuda and N. Sato : *ibid.*, May, 1981.
- Enrichment of Ti in Passivation Film on Fe-3Ti Alloy in Acidic Phosphate Solution ; M. Seo, M. Matsumura and N. Sato : *ibid.*, May, 1981.
- Measurement of Passivation Film on Iron in Phosphate Solution by Reflectometry ; K. Azumi, T. Ohtsuka, M. Seo and N. Sato : The Hokkaido Section Meeting of the Japan Inst. Met., June, 1981.

## CURRENT ACTIVITIES

- Critical Issue of Localized Corrosion; N. Sato: Seminar on the Local Corrosion and the Electrolytic Chemistry Sponsored by the Hokkaido Section of the Japan Inst. Met., July, 1981.
- Surface of Titanium; T. Ohtsuka: Seminar on the Grain Boundary Sponsored by the Hokkaido Section of the Japan Inst. Met., July, 1981.
- Properties of Tantalum Electrode Covered with Heat-Treated Anodic Oxide Film; T. Sakon, M. Seo, T. Ohtsuka and N. Sato: The Hokkaido Section Meeting of the Japan Chem. Soc., July, 1981.
- Surface and Corrosion of Metal; N. Sato: The 1st Seminar on Surface Science Sponsored by the Surface Science Soc. Japan, Aug. 1981.
- Passivity Breakdown and Pitting; N. Sato: The 8th Intern. Congr on Met. Corr., Mainz, FRG, Sept. 1981.
- Titanium Enrichment in Anodic Oxide Films on Fe-3%Ti Alloy; M. Seo, Y. Matsumura and N. Sato: *ibid.*, Sept. 1981.
- Auger Analysis of Passive Films on Iron-base and Nickel-base Alloys; M. Seo: Lecture at Centre National de la Recherche Scientifique, Paris, France, Sept. 1981.
- Ellipsometric Study of Passive Films on Titanium in Phosphate Solutions; M. Masuda, T. Ohtsuka and N. Sato: The 22nd Corrosion Science Symposium, Newcastle Upon Tyne, England, Sept. 1981.
- Anodic Oxide Film on HgTe and  $Hg_{0.8}Cd_{0.2}Te$  Compound Semiconductors; The 34th Symposium on Colloid and Interface Chemistry, Oct. 1981.
- Influence of Environmental Factors on Depth-Composition Profile of Passive Films on Iron- and Nickel-Base Alloys; M. Seo and N. Sato: The 44th Meeting of the Japan Chem. Soc., Oct. 1981.
- Analogy and Difference between the Passive Films on Iron, Nickel, and Cobalt; T. Ohtsuka and N. Sato: *ibid.*, Oct. 1981.
- Selective Ion Transport and Volume Flow through Precipitate Films of Corrosion Product; M. Sakashita and N. Sato: *ibid.*, Oct. 1981.

- Localized Corrosion of Metals; N. Sato: The Electrochemical Society-Ontario-Quebec Section Autumn Symposium, Ottawa, Canada, Oct. 1981.
- Passivity Breakdown and Pitting; N. Sato: Seminar in University of Nottingham, England, Oct. 1981.
- The Ion Selectivity of Rust Precipitates and Its Effect on the Corrosion of Metals in Aqueous Solution; N. Sato: Seminar at the Corrosion and Protection Centre in the UMIST, Manchester, England, Oct. 1981.
- Passive Films on Metals; N. Sato: Seminar at Centre National de la Recherche Scientifique, Paris, France, Oct. 1981.
- Passive Films on Iron, Nickel, and Cobalt; N. Sato: Seminar at the Corrosion Section in the National Research Council of Canada, Ottawa, Canada, Oct. 1981.
- Passivity Breakdown and Stability of Pitting; N. Sato: Seminar at the Pennsylvania State University, University Park, Pennsylvania, USA, Nov. 1981.
- Composition of Anodic Oxide Films on Fe-Ni Alloys in Strongly alkaline Solutions; Y. Sera, M. Seo and N. Sato: The Hokkaido Section Meeting of the Japan Inst. Met., Nov. 1981.
- AES Analysis of Passive Films on a Stainless Steel Containing Nb; C. -G. Kin, M. Seo and N. Sato: *ibid.*, Nov. 1981.
- Growth and Composition of Anodic Oxide Film on Fe-30Ni Alloy; M. Seo and N. Sato: The Autumn Meeting of the Japan Inst. Met., Nov. 1981.

## PHYSICAL METALLURGY LABORATORY

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

### *Students*

T. Kato, T. Ebe, Y. Takahashi, T. Ishikura, H. Nagato,  
K. Kurata, M. Osanai, M. Uchiyama,  
H. Iuchi and T. Katayama

Newly developed high voltage electron microscope (HVEM) of 1300 kV was installed last year. The HVEM is specially designed for studying irradiation damages in metals and alloys which will be used for future breeder and/or fusion reactors. The HVEM is designed for equipped with LaB<sub>6</sub> and W filaments, irradiation holders at high and low temperature, and other useful attachments. Environmental cell will be also provided for in situ experiments of gas-metal reaction, biological studies and others. Ultra high clean vacuum up to 10<sup>-6</sup> Pa and high resolution up to 0.144 nm can be achieved in this HVEM so as to give a powerful tool for microstructural studies in various fields such as physical, chemical and biological science in addition to the irradiation study on materials.

Also, an accelerator with 300 keV was installed this year. The accelerator can be used to irradiate the metals and alloys by H<sup>+</sup> and He<sup>+</sup> ions, which in near future will be connected with HVEM to perform dual beam irradiation experiment.

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 for fusion reactors. 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.

Prof. Takeyama attended the U. S.-Japan Seminar on Characteristics of Mechanical Properties of BCC Metals at Honolulu, U. S. A., in March to present the paper on hydrogen embrittlement\*<sup>1</sup>, and Japan-China Joint Meeting on Electron Microscope at Tairen, China, in August to present papers on Hydrogen Induced Micro-Crack\*<sup>2</sup> and Radiation-Induced Segregation\*<sup>3</sup>. Furthermore, in August Prof. Takeyama, Dr. Takahashi and Dr. Ohnuki attended the Second Topical Meeting on Fusion Reactor Materials at Seattle, U. S. A. to present three papers on Radiation-Induced Segregation in FCC\*<sup>4</sup>, BCC Alloys\*<sup>5</sup> and Stainless Steels\*<sup>6</sup>. After the conference they visited Hanford Engineering Development Laboratory, Lawrence Livermore National Laboratory and Berkeley, California University. Assist. Prof. Shibata attended 8th Int. Congress on Metallic Corrosion at Mainz, West Germany, in August to present a paper on Stochastic Process in Pitting Corrosion of 17% Cr Stainless Steels\*<sup>7</sup> and visited several institutes and universities in France to discuss his works. In November, Prof. Takeyama attended the International Conference on Neutron Irradiation Effects at Argonne, U. S. A., to present a invited paper on Effect of Substitutional and Interstitial Elements on Void Formation in Neutron-Irradiated Vanadium Alloys\*<sup>8</sup>. Prof. Takeyama, Dr. Takahashi and Dr. Ohnuki attended the Yamada Conference on point defects at Kyoto in November and presented three papers on radiation damage\*<sup>9-11</sup>.

### Oral Presentation

Corrosion Testing and Evaluation of Reliability; T. Shibata: The 3th Symposium on Probability Evaluation of Corrosion Phenomena, Mar. 1981.

Corrosion as a Probability Phenomena; T. Shibata: Meeting on Consideration of Corrosion Strength, Ohsaka Univ., Mar. 1981.

A Study of New materials Development for First Wall on Fusion Reactor; T. Takeyama: Research Meeting on Fusion Reactor, Mar. 1981.

## CURRENT ACTIVITIES

- Nucleation of Crack and Micro-Structure Induced by Hydrogen ;  
H. Takahashi and T. Takeyama : U. S.- Japan Seminar on  
Characteristics of Mechanical Properties of BCC Metals ; U.S.A.,  
Mar. 1981.\*1
- The behavior of Irradiation-Induced Secondary Defect Clusters for  
Ag-Dilute Cu Alloy by HVEM ; H. Takahashi and K. Urban ;  
Research Meeting on Fundation and Application of Electron  
Microscopy with Atomic Level, Hiroshima, Mar. 1981.
- Phase Transformation of C<sup>+</sup> ions Irradiated Fe-13% Cr Alloys ;  
S. Ohnuki, H. Takahashi and T. Takeyama : The 56th  
Spring Meeting of the Japan Institute of Metals, April, 1981.
- Void Formation in Fe-Mo Alloy and Fe by Electron Irradiation ;  
S. Maruyama, S. Ohnuki, H. Takahashi and T. Takeyama :  
*ibid.*, April, 1981.
- The Process of Probability of Pits in 17Cr Stainless Steel ; T.  
Shibata and T. Takeyama : *ibid.*, April, 1981.
- The role of Ti and Mo for Resistace Improvement of Pitting in  
17Cr Stainless Steel ; T. Shibata, T. Takeyama and H.  
Ohmori : The Hokkaido Section Meeting of the Japan Institute  
of Metals, Nov. 1981.
- The Estimation of Maximum Value of Pitting Depth for Bottom  
Plate of Oil Tank by Analysis of Extrem Value ; T. Shibata,  
K. Okamoto : The Annual Meeting of Corrosion Research  
Association, May 1981.
- The Problem and the Existing state for Irradiation Study by HVEM ;  
T. Takeyama : The Kanto Section Meeting of the Japan  
Institute of Metals, June 1981.
- Creep Deformation of Mo ; T. Takeyama, H. Takahashi and S.  
Wazima : The Sympodium on Refractory Metals, June 1981.
- Irradiation-Induced Segregation at Grain Boundary ; T. Takeyama :  
The Hokkaido Section Meeting of the Japan Institute of Metals,  
July 1981.
- Radiation-Induced Segregation at Internal Sinks in Electron Irradi-  
ated Binary Alloys ; T. Takeyama : The Meeting of Japan-  
China on Electron Microscope, China, Aug. 1981.\*2
- Nucleation of Micro-Crack and Void Induced by Hydrogen in Iron

- and Steel; T. Takeyama: The Meeting of Japan-China on Electron Microscope, July 1981.\*3
- Radiation-Induced Segregation at Internal Sinks in Electron Irradiated Binary Alloys; H. Takahashi, S. Ohnuki and T. Takeyama: Second Topical Meeting on Fusion Reactor Materials, U. S. A., Aug., 1981.\*4
- Void Swelling and Microchemical Segregation in Ion-Irradiated 316 Stainless Steel; M. Terasawa, S. Nakahigashi, T. Takeyama, S. Ohnuki and H. Takahashi: *ibid.*, Aug., 1981.\*6
- Void Swelling and Segregation of Solute in Ion-Irradiated Ferritic Steels; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid.*, Aug., 1981.\*5
- Strain Electrode of in High Temperature and High Pressured Water; T. Shibata: The Seminar on Metals Corrosion in High Temperature and High Pressured Water. Aug. 1981.
- Death and Birth Stochastic Process in Pitting Corrosion of 17 Cr Ferritic Stainless Steels; T. Shibata and T. Takeyama: 8th Int. Congr. on Metallic Corrosion, W. Germany Aug. 1981.\*7
- The Influence of Hydrogen for Irradiation-Induced Segregation in Materials; T. Takeyama: The Meeting on Fusion reactor Materials, Sept. 1981.
- Void Swelling and Irradiation-Induced Segregation of 20% cold rolled 316 Stainless Steel; S. Nakahigashi, T. Terasawa, T. Takeyama, H. Takahashi and S. Ohnuki: The 89th Meeting of the Japan Institute of Metals, Nov., 1981
- Phase Change and Void Formation in Ion-Irradiated Fe-13%Cr Alloy; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid.*, Nov., 1981.
- Voids Formation in Neutron-Irradiated Vanadium Based Alloys; H. Takahashi, S. Ohnuki and T. Takeyama: *ibid.*, Nov., 1981.
- The Influence of Ti on Void Formation in Fe-Ti Alloys; T. Kato, H. Takahashi, S. Ohnuki and T. Takeyama: *ibid.*, Nov., 1981.
- The Role of Ti and Mo and Death-Birth Stochastic Process in Pitting Corrosion of 17Cr Stainless Steel; T. Shibata and T. Takeyama: *ibid.*, Nov., 1981
- Effect of Substitutional and Interstitial Elements on Void Formation

## CURRENT ACTIVITIES

- in Neutron-Irradiated Vanadium Alloys; T. Takeyama, H. Takahashi and S. Ohnuki: Inter, Conf. on Neutron Irradiation Effects, U. S.A., Nov., 1981.\*<sup>8</sup>
- The Mobility of Vacancies and Interstitials in Ag-Cu Studied by High Voltage Electron Microscopy; H. Takahashi and K. Urban: Yamada Conf. on Point Defects and Defect Interactions in Metals, Japan, Nov., 1981.\*<sup>9</sup>
- Effect of the Interaction Between Solute Atoms and Defects on Formation of Defect Clusters; H. Takahashi, T. Takeyama, S. Ohnuki and T. Kato: *ibid.*, Nov., 1981.\*<sup>10</sup>
- Radiation-Induced Segregation at Internal Defect Sinks in Electron-Irradiated FCC Alloys; S. Ohnuki, H. Takahashi and T. Takeyama: *ibid.*, Nov., 1981\*<sup>11</sup>
- Effect of Si-Segregation on Void Formation in Ni-Si Alloys; T. Ebe, H. Takahashi and T. Takeyama: The Hokkaido Section of the Japan Institute of Metals, Nov. 1981.

## ELECTROMETALLURGY LABORATORY

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

### *Students*

S. Ajimura, K. Orita, S. Ohta, M. Okazaki, M. Okadera,  
H. Kudo, M. Chida and A. Murasawa

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. Viscosity of these molten salts and volatile species from the melts are being measured in this temperature range for cell design and operation analysis.

(2) The rotating bipolar electrode cells are developed to remove heavy metals electrochemically from the waste water on metallurgical processes and the fundamental function of the cells are being studied in dilute cupric sulfate solution.

(3) The study of corrosion and inhibition mechanisms of zinc and aluminum by several organic inhibitors in chloride solutions is conducting using gravimetric and electrochemical techniques. Benzotriazole and its derivatives, effective and widely used corrosion inhibitors for copper and copper alloys, were used as inhibitors for the metals with special emphasis placed on their application to multi-metal systems, i. e., solar heating and cooling systems. It was found that these compounds are good inhibitors in the wide range of pH and adsorbed mainly at the cathodic reaction sites of the metals. In the acidic media acceleration of corrosion was observed in the dissolution of zinc in the presence of the inhibitors. Coloring phenomenon was also observed in the process of dissolution of both zinc and aluminum in hydrochloric acid containing

## CURRENT ACTIVITIES

benzotriazole and its related compounds.

(4) In order to elucidate the effects of micro-vibration on the corrosion of pipe-line materials, some fundamental corrosion tests are carried out under controlled conditions of vibrating.

### Oral Presentation

Benzotriazole as a Corrosion Inhibitor for Zinc; T. Notoya and T. Ishikawa: The 1981 Winter Meeting of the Hokkaido Section of the Japan Chemical Society, Jan., 1981.

An Estimation Method for the Performance of Rotating Bipolar Electrode Cell in Extraction of Copper Ions from Dilute Solutions; K. Orita, T. Sasaki and T. Ishikawa: The 7th Hokkaido Section Meeting of Electrochem. Soc. of Japan, Jan., 1981.

A Resistance for Chlorine Gas Evolution on Various Carbon Anode during Electrolysis of Chloride Melts; M. Itatsu, S. Konda and T. Ishikawa: *ibid.*, Jan., 1981.

Continuous Measurement of Corrosion Rate in Alkali Nitrate Melts; T. Sasaki, S. Mikami and T. Ishikawa: The 16th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1981.

Effect of Micro-Vibration of the Specimen on its Corrosion Rate of Mild Steel immersed in Various Neutral Solutions; M. Murakami and T. Ishikawa: *ibid.*, Jan., 1981.

Effect of Porosity of Wall Materials on the Cell Efficiency of Bipolar Electrode Cell; T. Ishikawa and S. Konda: The 48th Annual Meeting of the Electrochem. Soc. of Japan, March, 1981.

Behaviour of Chlorine Evolution on Various Carbon Anode during Electrolysis of Molten Salt containing Aluminum Chloride; S. Konda, M. Itatsu and T. Ishikawa: *ibid.*, March, 1981.

Corrosion Inhibition of Zinc by Benzotriazole Derivatives; T. Notoya and T. Ishikawa: The 43rd Annual Meeting of Japan Chemical Society, April, 1981.

Inhibitive Action of Benzotriazole to Zinc Corrosion; T. Notoya and T. Ishikawa: The Spring Meeting of the Japan Institute

- of Metals, April, 1981.
- Corrosion Inhibition and Acceleration of Zinc by Benzotriazole and Its Derivatives; T. Notoya and T. Ishikawa: '81 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1981.
- Effect of Sine-Wave Vibration on the Corrosion of Mild Steel in Neutral Aqueous Solutions; T. Ishikawa and M. Murakami: *ibid.*, May, 1981.
- Corrosion Inhibitive Action of Benzotriazole and Its Derivatives; T. Notoya: Seminar on Corrosion Inhibitors by Japan Association of Corrosion Control, May, 1981.
- On the New Smelting Processes of Aluminum; T. Ishikawa: The Spring Meeting of Hokkaido Section of JIM., June, 1981.
- On Prevention of Dezincification of Brasses by Corrosion Inhibitors; T. Notoya: The 1st Meeting of the Special Committee for Studying Copper Alloy Corrosion, Aug., 1981.
- Continuous Measurement of Corrosion Rate and Corrosion Loss in Molten Salt Systems; T. Ishikawa and T. Sasaki: The 8th International Congress on Metallic Corrosion (Mainz), Sept., 1981.
- Electrochemical Treatment of Cupric Sulfate Solution with Rotating Bipolar Electrode Cell (Part 2) Effect of Rotating Frequency and Solution Flow Rate to Metal Deposition; K. Orita, T. Sasaki and T. Ishikawa: The 1981 Fall Meeting of Electrochem. Soc. of Japan, Oct., 1981.
- Experimental Study of the Equivalent Circuit Components for Discoidal Bipolar Electrode; T. Sasaki and T. Ishikawa: *ibid.*, Oct. 1981.
- Volatile Species of Various Chloride Melts containing Aluminum Chloride at 800°C; S. Ajimura, S. Konda and T. Ishikawa: *ibid.*, Oct., 1981.
- Electrowinning of Liquid Aluminum by using Funnel-Pile Type Bipolar Electrode Cell (Part 8) A Modified Procedure for Analysis of the Working Cell; T. Ishikawa: The 15th Symposium on Molten Salt Chemistry, Nov., 1981.
- Electrowinning of Liquid Aluminum by using Funnel-Pile Type

## CURRENT ACTIVITIES

Bipolar Electrode Cell (Part 9) Effect of Cell Lining Materials on the Cell Efficiency of the Bipolar Electrode Cell; S. Konda and T. Ishikawa: *ibid.*, Nov., 1981.

Some Problems on the Application of Resistometry to Continuous Measurement of Corrosion Rate in Molten Salt Systems; T. Sasaki and T. Ishikawa: *ibid.*, Nov., 1981.



## ENGINEERING MACHINERY MATERIALS LABORATORY

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

### *Students*

H. Tsushima, T. Terada, T. Nakamura, K. Ōkubo, T. Narita,  
T. Kikuchi, K. Shirakawa, J. Nagai, J. Nishio,  
M. Funaki, T. Mishima, Y. Murayama  
and M. Kamide

Assistant Professor T. Noguchi had received doctorate of engineering from Hokkaido University in June 1981. The title of thesis was "Research on Strength Characteristics of Cast Iron and Its Evaluation."

Subjects of research in progress in this laboratory are as follows:

(1) Measurement of fracture toughness of flake graphite cast iron was carried out with standardized methods for steel and other metals. Results showed there are such problems due to the non-elastic behavior of this material as no effect of thickness, increasing of the value with increasing of tensile strength and ductile microfractographs on brittle fracture surface.

(2) Propagation of crack in low cycle fatigue of flake graphite cast iron was observed by cyclic bending test. Though the results scattered remarkably, each curve of crack propagation was able to be expressed by a function  $da/dN=C(\Delta K)^n$  in linear fracture mechanics.

(3) Notch strength of sintered steel was measured with round bar and plate, and the results were analyzed on the stress distribution obtained by FEM. At room temperature no effect was found with the round bars, though the effect was apparent in the plates. At liquid nitrogen temperature both specimens showed decrease

## CURRENT ACTIVITIES

of strength remarkably. The results were well explained by the over stressed depth theory induced in this laboratory.

Scattering of tensile strength of sintered steel was also studied statistically using Weibull sheets. There appeared marked difference in strength distribution according to the test temperature and type of fracture.

(4) Effect of nodule size on the impact strength of S. G. iron was tested at various temperature. The results showed that iron with small graphite nodules had low fracture energy at upper shelf and high energy at lower shelf on the Charpy-energy vs. temperature curve.

(5) Effect of nodule size on the growth of S. G. iron was examined. At early stage the growth of iron with small graphite nodules was greater than that of iron with large nodules, though at late stage of the growth the relation changed reversely.

(6) As a basic experiment for a surface hardening method of sintered steel, specimens made of pressed powder of iron with 3% graphite powder were heated in the atmosphere of low oxygen concentration. It was observed clearly that the surface of sintered iron heated in less than 2% oxygen concentration was hardened after quenching.

(7) Effect of oxygen concentration on the growth of flake graphite cast iron was examined in austenite region of heating. Results showed non-proportional increase of growth against the oxygen concentration and the remarkable increase at less than 2% oxygen.

## Oral Presentation

Fracture Criterion of Flake Graphite Cast Iron; T. Noguchi:  
The 30th Lecture Meeting of Japan Society of Material Science.  
(Kyoto) May 1981.

Effect of Oxygen on the Growth of Flake Graphite Cast Iron;  
M. Sōma and K. Nagaoka: The 99th Grand Lecture Meeting  
of the Japan Foundrymen's Society. (Tokyo) May 1981.

Effect of Annular Ribs on the Bending Strength of Cast Iron Disk;

- T. Noguchi, T. Narita and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society. (Kushiro) July 1981.
- Fracture Toughness Measurement of Cast Iron; T. Noguchi, T. Terada and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society. (Kushiro) July 1981.
- Fracture Toughness of Flake Graphite Cast Iron; T. Terada, T. Noguchi and K. Nagaoka: The 33rd Hokkaido Section Lecture Meeting of the Japan Society of Mechanical Engineers. (Kitami) 1981.
- Notch Strength of Sintered Steel; E. Tsushima, T. Noguchi and K. Nagaoka: The 33rd Hokkaido Section Lecture Meeting of the Japan Society of Mechanical Engineers (Kitami) 1981.

**NONFERROUS EXTRACTIVE METALLURGY  
LABORATORY**

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

***Students***

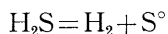
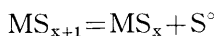
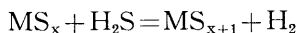
K. Funaki, R. Togashi, Y. Nakai, G. Kanō, T. Mōri,  
M. Noda, T. Ōmi and M. Yamaguchi

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

(1) New development in the hydrogen production technology without using fossil fuels.

i) Thermochemical splitting of hydrogen sulfide.

Thermochemical splitting of  $H_2S$  by the following two combination is being carried out



ii) Pyrohydrolysis of metal chlorides.

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

iii) Hydrogen production by using water and sulfur or sulfur compounds. Reaction between steam and a metal sulfide such as  $Ag_2S$ ,  $CaS$ , and  $FeS$  are being investigated within the temperature range  $700 \sim 1000^\circ K$ .

(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 lime 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 or solar energy 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 electrocyte. 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

Recovery of Hydrogen from Hydrogen Sulfide with Metal Sulfide ;

H. Kiuchi, K. Funaki and T. Tanaka : The Winter Meeting of the Hokkaido Sections of the JSAC and JCS, Feb. 1981.

Pyrohydrolysis of Metal Chlorides (II) ; R. Shibayama, N. Tsuchida and T. Tanaka : *ibid.*, Feb. 1981.

Hydrogen Reduction of Copper Sulfate in Sulfuric Acid Solution ; R. Togashi and T. Nagai : *ibid.*, Feb. 1981.

Fundamental Studies on the Reaction between Metal Chloride and Steam (VI) ; R. Shibayama, N. Tsuchida and T. Tanaka : Annual Meeting of Min. Met. Inst. Japan, April 1981.

Removal of Arsenic from the Hot Waste Water from Geothermal Plants by Hydrated Zirconium Oxide ; R. Togashi and T. Nagai : *ibid.*, Apr. 1981.

Hydrogen Reduction of Copper Electrolyte ; R. Togashi and T. Nagai : *ibid.*, Apr. 1981.

## CURRENT ACTIVITIES

- A Study on the Utilization of Hydrogen Sulfide (VII); H. Kiuchi, K. Funaki and T. Tanaka : *ibid.*, Apr. 1981.
- Effect of HCl gas on the Reduction of Metal Sulfates with Hydrogen ; R. Shibayama, K. Ise and T. Tanaka : The Spring Meeting of the Hokkaido Section of the Min. Met. Inst. Japan, June 1981.
- Thermochemical Decomposition of Hydrogen Sulfide with Molten Bismuth ; H. Kiuchi, Y. Nakai and T. Tanaka : *ibid.*, May 1981.
- Purification of Copper Electrolyte by Hydrogen Sulfide ; T. Nagai and R. Togashi : *ibid.*, May 1981.
- Action of Metal Sulfide on the Thermal Dissociation of Hydrogen Sulfide (V); H. Kiuchi, K. Funaki and T. Tanaka : The Hokkaido Section Meeting of JIM and ISIJ, June 1981.
- Properties of the Copper Powder from Hydrogen reduction of Copper Electrolyte ; *ibid.*, June 1981.
- Reduction of Metal Sulfate with the Pyrohydrolysis Gas of  $\text{FeCl}_2$  ; R. shibayama, K. Ise and T. Tanaka : The 1981 Summer Meeting of the Hokkaido Section of the Japan Chem. Soc., July 1981.
- A Study on the Thermal Decomposition of Hydrogen Sulfide with Molten Metals (II); H. Kiuchi, Y. Nakai and T. Tanaka : *ibid.*, July 1981.
- Application of Hydrogen to the Treatment of Sulfides Ores ; T. Tanaka, R. Shibayama and H. Kiuchi : Fall Meeting of the Min. Met. Inst. Japan, Aug. 1981.
- Fixation of Sulfur by the Thermochemical Decomposition of Hydrogen Sulfide ; T. Tanaka, H. Kiuchi and R. Shibayama : *ibid.*, Aug. 1981.
- Hydrogen Energy and Metallurgy ; T. Tanaka : Annual Meeting of Government Industrial Development Laboratory, Hokkaido, Nov. 1981.

## Electrochemical Passivation of Metals

N. Sato and G. Okamoto

Comprehensive Treatise of Electrochemistry Vol. 4,

Edited by J. O'M. Bockris, B. E. Conway

E. Yeager and R. E. White, Plenum

Publishing Corp., p. 193 (1981)

This review paper describes the recent progress in metallic passivity and passive films on metals.

1) Potentiostatic anodic polarization curves. 2) Active-passive transition. 3) Passive films. 4) Dissolution of passive metals. 5) Theory of passivity 6) Chemical breakdown of passive films. 7) Transpassive dissolution 8) Electron transfer reactions at passive metal electrodes. 9) Concluding Remark (English)

**Metallic Corrosion Fundamentals**

— Surface Electrochemistry of Metals —

N. Sato

Bull. Japan Inst. Metals, **20**, No. 8, 712 (1981);

No. 9, 794 (1981); No. 10, 871 (1981);

No. 11, 935 (1981)

This lecture paper provides a comprehensive text of corrosion fundamentals for engineers and graduate course students in Universities. 1) Corrosion and electrochemistry. 2) Electrochemical potential. 3) Electrode potential. 4) Diffusion potential. 5) Membrane potential. 6) Electrode reaction. 7) Equilibria of corrosion reactions. 8) Kinetics of corrosion reactions. (Japanese)



## **Thermodynamics of Metallic Corrosion in Aqueous Solution**

N. Sato

PETROTECH 4, No. 3, 262 (1981)

This lecture paper describes the chemical and electrochemical equilibria of corrosion reactions consisting of anodic metal oxidation and cathodic oxidant reduction in aqueous solutions. 1) Reaction at the Metal/solution interface. 2) Metal ions in aqueous solution. 3) Formation of corrosion product precipitates. 4) Formation of oxide films on metals. 5) Equilibrium diagrams for metallic corrosion. 6) Localized corrosion and corrosion diagrams. (Japanese)

**Kinetics of Metallic Corrosion in Aqueous Solution**

N. Sato

PETRORECH, 4, No. 3, 262 (1981)

This lecture paper provides an introduction to corrosion kinetics. 1) Electrochemical theory of metallic corrosion. 2) Polarization curves (potential-current curves) of anodic metal dissolution and cathodic oxydant reduction on metals. 3) Kinetics of homogeneous corrosion. 4) Passivation of metals. 5) Local cell corrosion due to aeration. 6) Repassivation of metals. 7) Crevice corrosion. 8) Corrosion product precipitates on metals. (Japanese)

## Introduction to Corrosion Protection

N. Sato

Text at 1981 Short Corrosion Course in the  
Hokkaido Corrosion Research  
Association, p. 14 (1981)

This lecture introduces a primary approach to the corrosion and corrosion control for managers and engineers working in bridge construction. 1) Why do metals corrode? 2) Some metals can be used as fuel for metal fuel cell. 3) Combustion of metals produces energy, which can be converted to electricity in fuel cells or merely dissipated away with corrosion. 4) Sites for metal dissolution and for oxygen reduction on the metal surface are often localized to cause localized corrosion. 5) Crevice corrosion occurs when oxygen is depleted in crevices. 6) Galvanic corrosion of less noble metals occurs when less noble metals contacts to more noble metals. 7) The active and passive states of metal surfaces. 8) Electrical methods of metal protection. (Japanese)

**Corrosion and Passivation of Metals**

N. Sato

Kagaku Kogaku (Chemical Engineering),  
45, 448 (1981)

This lecture paper introduces general aspects of metallic corrosion and passivation to Chemical Engineers. 1) Main environmental factors affecting corrosion of metals. 2) The state of metal surface determining corrosion. 3) The state of metal surface determined by environments. 4) Stability of the passive state. 5) Anti-breakdown property of passive surface films on metals. 6) Repassivation at film breakdown sites on metals. 7) Anti-corrosivity of metallic materials. (Japanese)

## **Metal Surface and Corrosion**

N. Sato

Text for the 1st Seminar on Surface Science  
Sponsored by the Surface Science  
Soc. Japan, p. 57 (1981)

This review paper describes the recent progress in physical chemistry of metal surfaces in relation to corrosion. 1) Segregation of impurity elements at the metal surface from the metal interior. 2) Adsorption of gaseous molecules on the metal surface. 3) Thermodynamics of metal surfaces. 4) Formation of surface oxide films on metals. 5) Breakdown and reformation of surface oxide films on metals in gaseous environments. 6) Surface adsorption on metals in aqueous solution and electrical double layer. 7) Dissolution and anodic oxidation of metals in aqueous solution. 8) Breakdown and reformation of surface oxide films on metals in aqueous solution. (Japanese)

## Recent Progress in Corrosion Science

N. Sato

Report in the 100th Meeting of the Corrosion and  
Protection Committee in the Society of  
Materials Science, Japan, Vol. 20,  
Part 1, p. 101 (1981)

This paper reviews the progress in corrosion science that has been made in the past ten years. 1) Electrochemical methods for corrosion rate measurements. 2) Passivation and passive films. 3) Role of corrosion product precipitates on metal in the corrosion processes. 4) Passivity breakdown and localized corrosion. 5) Application of fracture mechanics to the study of stress corrosion cracking. 6) High temperature oxidation of metals and alloys. 7) High temperature water corrosion of metals. (Japanese)

## Passive Films on Iron in Phosphate and Borate Solutions

R. Nishimura, K. Kudo and N. Sato

J. Japan Inst. Met., 45, No. 5, 461 (1981)

The passive films formed on iron in neutral, alkaline phosphate and alkaline borate solutions were investigated by using electrochemical and ellipsometric techniques. Chemical analyses of iron ion dissolved from the film and ellipsometric measurements of  $\delta P-\delta A$  curve during galvanostatic cathodic film reduction have shown that the passive films formed in these solutions consist of a deposit layer next to the solution and a barrier layer in contact with the metal. The oxidation state of iron ion in the deposit layer is in the iron (III) state and is scarcely affected by pH and anions in the solution. The barrier layer composition, however, depends on pH and anion species. In borate solutions, the barrier layer composition changes from ferric oxide (pH 8.42) to magnetite-like oxide (pH 11.50) with increase of solution pH. On the other hand, its composition in phosphate solutions contains iron (II) ions giving rise to the mean oxidation valency,  $Z_{Fe}=2.33$  in the pH range of 0.42 to 12.60. It has been found that depletion or enrichment of iron ions occurs at the deposit/barrier layers interface in borate solutions of pH 8.42 and 11.50 with the degree of depletion or enrichment being dependent on pH. No iron depletion or enrichment, however, is found in the passive films formed in phosphate solutions. The results are explained in terms of the ion permselective property of the passive films formed in phosphate and borate solutions. (Japanese)

## Passive Films on Iron in Acidic Phosphate Solutions

R. Nishimura and N. Sato

J. Japan Inst. Met., 45, No. 9, 908 (1981)

The composition, structure and thickness of passive films on iron in acidic phosphate solutions of pH 1.85 to pH 5.90 have been investigated as a function of electrode potential by using ellipsometric and electrochemical techniques. From ellipsometric measurements of  $\delta P$ - $\delta A$  curves during galvanostatic-cathodic film reduction, it is found that the passive film consists of a barrier layer and a deposit layer and that the latter layer disappears in the pH region below pH 2. Below pH 5.5, the former layer can be divided into two layers; an outer layer and an inner layer. The outer barrier layer thickness decreases with increasing pH and becomes zero at pH 5.5. At a constant overpotential of anodic oxide formation, the total thickness of the barrier layer tends to increase with increasing pH. Chemical analyses of iron ion dissolved from the film during the cathodic reduction have shown that the deposit layer exhibits no change in its composition with pH and that the composition of the inner barrier layer differs from that of the outer barrier layer, the former showing the mean oxidation state of  $Z_{Fe} \doteq 2.67$  and the latter the mean oxidation state of  $Z_{Fe} \doteq 3.00$ , irrespective of the electrode potential and pH. Enrichment of iron ions is found to occur at the inner barrier-outer barrier layer interface as well as at the interface between the outer barrier layer and the deposit layer. The electric field that occurs in the barrier layer at the steady state is estimated to be  $1 \times 10^9 \text{ V} \cdot \text{m}^{-1}$  in the inner barrier layer and  $3 \times 10^8 \text{ V} \cdot \text{m}^{-1}$  in the outer barrier layer of the passive film in phosphate solution at pH 1.85. (Japanese)



## Effects of Formation Procedure and Anion on Passive Films on Passive Films on Iron in Neutral Solution

R. Nishimura and N. Sato

Corrosion Engineering (Boshoku Gijutsu),  
30, No. 8, 456 (1981)

The composition, structure and thickness of passive films formed on iron by anodic oxidation in two steps with a preliminary oxidation at pH 11.50 followed by one hour oxidation in borate or phosphate solution at pH 8.42 have been investigated by the use of ellipsometric and electrochemical techniques, and the results are compared with those of passive films formed by a direct oxidation in the same solution. Chemical analyses of iron ion dissolved from the film and ellipsometric measurements of the film during galvanostatic cathodic film reduction reveal that, irrespective of its formation procedure, the passive film is a two-layer film consisting of a deposit layer next to the solution and a barrier layer in contact with the metal. In borate solution, the compositions and the optical constants of the deposit and barrier layers exhibit almost no difference with different oxidation procedures, except for a minor difference in the barrier layer formed at less noble potential. In phosphate solution, the deposit layer composition is scarcely affected by oxidation procedure, but the barrier layer composition differs in different oxidation procedures with an Fe(II) ion-rich oxide in direct oxidation and a magnetite-like oxide in two step oxidation. The optical constants of the deposit and barrier layers and the ion enrichment at the deposit/barrier interface are found to depend on the oxidation procedure. The thickness of the deposit layer formed by direct oxidation is always thicker than that of the deposit layer formed by two step oxidation, but the barrier layer thickness is determined solely by the overpotential applied regardless of the oxidation procedure. The results are explained in terms of the ion selective property of the film, which differs in different oxidation procedures. (Japanese)

## Two-Layer Formation of Passivating Films on Cobalt in Neutral Solution

T. Ohtsuka and N. Sato

J. Electrochem. Soc., **128**, No. 12, 2522 (1981)

Layer structure and thickness of passivation oxide films on cobalt have been investigated at stationary and transient states in solution of  $0.30 \text{ mol dm}^{-3}$  boric acid —  $0.075 \text{ mol dm}^{-3}$  sodium borate mixture of pH 8.4 by means of chemical analysis and *in situ* ellipsometry combined with electrochemical measurements. A two-layer structure composed of an inner CoO and an outer  $\text{Co}_{3-x}\text{O}_4$  is found in a potential range more positive than 0.75 V (vs. the hydrogen electrode at the same solution). The nonstoichiometry changes from  $x=0$  to 0.33 with increasing anodic potential. The outer  $\text{Co}_{3-x}\text{O}_4$  layer thickness increases linearly with potential, whereas the inner layer thickness is not a simple function of potential, but depends on the film formation procedure. A step-wise potential increase gives an initial rapid growth of the outer  $\text{Co}_{3-x}\text{O}_4$  layer followed by a gradual thickening of the inner CoO layer. The transient film growth behavior is interpreted in terms of a field-assisted ion diffusion mechanism, and the self-diffusion coefficient in the inner CoO layer is estimated to be  $D/\text{cm sec}^{-1} = 6.5 \times 10^{-21} \sim 2.6 \times 10^{-20}$ . (English)

**Duplex Oxide Film Formation on Elemental Metals  
by Cation Interstitial Diffusion**

A. T. Formhold, Jr. and N. Sato

Physics Letters, **84A**, No. 4, 219 (1981)

A theory for the simultaneous formation of two oxide phases on an elemental metal under diffusion-controlled conditions has been developed which enables the determination of quasi-steady-state growth kinetics following step function changes in the experimental conditions of ambient temperature or oxygen partial pressure.  
(English)

**Ellipsometric Study of Corrosion Resisting  
Passivation Films on Stainless Steel**

N. Sato, M. Seo and T. Ohtsuka

Report of Research Project, Grant in Aid for Scientific  
Research, Project Number 447049,  
Hokkaido University, 1981

A new apparatus was constructed which allowed both ellipsometry and reflectometry to be applied to the measurement of a protective oxide film on a metal surface in aqueous solution. From the change in the three independent relative reflectivity observed during the formation of a surface film, one can determine the complex refractive indices and the thickness of the thin surface film simultaneously. This method has been applied to the measurement of the passive film formed on iron in phosphate solutions at pH 1.6, 3.1, and 4.3 and in borate solution at pH 8.4, and on nickel in sulphate solutions at pH 0.1, 0.9, and 1.6.

For iron, the thickness of the passive film was found to increase linearly with anodic potential. The film thickness for unit volt and hence the average field strength in the film, however, depend on the electrolytic pH. The relation between the anodic current at steady state and the mean electric field strength in the film is found to obey the Cabrera-Mott equation.

For nickel, it was found that the thickness and the refractive index of the passive film depend on the electrode potential non-monotonously. From the measured value of the complex refractive indices it is likely that the passive film is a partially hydrated nickel oxides,  $\text{NiO}_{1+x}(\text{H}_2\text{O})_y$ , with the nonstoichiometry  $x$  and the degree of hydration  $y$ , both of which change with the electrode potential. (Japanese)

## Passivity Breakdown and Pitting

N. Sato

Proceedings of The 8th Intern. Congr. Met.  
Corr., Vol. 3, p. 2053 (1981)

A model of electrocapillary breakdown of passive films predicts that the film breakdown occurs above a critical electrode potential. It is also predicted from the film dissolution kinetics that above a certain potential the passive film is electrochemically unstable undergoing the potential-dependent transpassive dissolution. The film breakdown does not necessarily lead to pitting. The stability of pitting is determined by the local ion build-up in the pit and there is a critical ion concentration (about  $2 \text{ mol} \cdot \text{dm}^{-3}$  for stainless steel) above which stable pit growth occurs. This critical ion concentration appears to correspond for brightening pits to the lowest aggressive anion concentration required for the transition from etching dissolution to electrobrightening dissolution of metals and for etching pits to the lowest hydrogen ion concentration for depassivation. The local ion concentration at the metal surface is proportional to the product of the diffusion layer thickness  $\delta$  and the metal dissolution rate  $i$ . Since  $\delta$  is limited by convection ( $\delta < 0.5 \text{ mm}$ ), the dissolution rate  $i$  less than a certain value ( $i < 0.1 \text{ A} \cdot \text{cm}^{-2}$ ) does not cause stable pitting to develop on the flat metal surface, even if the local breakdown of the passive film occurs. (English)

**The Stability of Pitting Dissolution of Metals  
in Aqueous Solution**

N. Sato

Corrosion and Corrosion Protection (Proceedings of An  
Intern. Symp. Honoring Professor H. H. Uhlig on  
His 75th Birthday), Ed. by R. P. Frankenthal  
and F. Mansfeld, The Electrochem. Soc.,  
Inc., Pennington, NJ, p! 101 (1981)

The stability criteria of pitting dissolution of metals are examined on the basis of recent results. Pitting dissolution is stable, if the local ion concentration build-up at pit sites exceeds a certain critical value, which for pits at noble potentials appears to correspond to the lowest ion concentration required for the transition from etching dissolution to brightening dissolution. The smallest pit size for stable pitting decreases with anodic potential, and hence the larger defect on the metal surface gives rise to the less noble pit initiation potential. The local pH at pit sites seems to contribute to the initiation of etching pits at less noble potentials, whereas the stability of brightening pits at noble potentials is determined by the local concentration of aggressive anion. The metal dissolution rate less than a certain value ( $\sim 0.1 \text{ A cm}^{-2}$ ) does not produce sufficient ion build-up for the initiation of stable pits on the flat metal surface. (English)

**Composition and Structure of Anodic Oxide Films  
on Copper in Neutral and Weakly  
Alkaline Borate Solutions**

M. Seo, T. Iwata and N. Sato

Bulletin of the Faculty of Engineering, Hokkaido  
University, No. 102, 93 (1981)

Copper surfaces anodically oxidized at constant potential for 1 h in deaerated neutral and weakly alkaline borate solutions were examined by using electrochemical techniques combined with Auger electron spectroscopy (AES) and X ray-photo electron spectroscopy (XPS). The thickness (1~4 nm) of anodic oxide films coulometrically estimated decreased with increasing anodic potential in the active region but increased in the passive region, irrespective of the solution pH. The anodic oxide films formed on copper in the passive region consisted of  $\text{Cu}_2\text{O}$  as an inner layer and of partly hydrated cupric oxide,  $\text{CuO}_x(\text{OH})_{2-2x}$  as an outer layer. Dehydration of the outer layer progressed with the increasing anodic potential. The active potential region of copper was divided into two parts;  $\text{Cu}_2\text{O}$  film was directly formed on copper without any dissolution of cuprous ions in active region 1 whereas in active region 2 the formation of  $\text{Cu}_2\text{O}$  and the dissolution of cupric ions proceeded simultaneously.

Discussion was made on the formation mechanism of the outer layer in the passive region and on the dissolution mechanism of  $\text{Cu}_2\text{O}$  in the active region. (English)

**Titanium Enrichment in Anodic Oxide Films  
on Fe-3%Ti Alloy**

M. Seo, Y. Matsumura and N. Sato

Proceedings of The 8th Intern. Congr. Met.

Corr., Vol. 1, p. 108 (1981)

Enrichment of titanium in the surface oxide films during anodic oxidation of Fe-3% Ti alloy in pH 3.0 phosphate solution was investigated to examine the effect of alloying titanium on the corrosion resistance of iron. The three per cent-addition of titanium reduced the passivity-maintaining current density of iron to one-fifth. Titanium was enriched markedly in the anodic oxide films formed on Fe-3% Ti alloy. A significant amount of phosphor originated from the solution was distributed in the whole range of the film thickness. Both the amount of titanium enriched in the film and the film thickness increased, as the amount of electric charge required for passivation was greater. The most part of the electric charge for passivation was the one that passed when the alloy was subjected to active dissolution before passivation. Atomic absorption analysis of the solution revealed preferential dissolution of iron as ferrous ions in the active potential region. Passivated electrodes of Fe-3% Ti alloy and of pure iron, however, exhibited almost the same potential-decay under the open-circuit condition in the solution.

From the results discussions were made on the mechanism of film formation and on the role played by a titanium-enriched film in passivation. (English)



**Impedance Measurement of Anodic Oxide Films  
by Frequency Response Analyzer**

M. Nagayama, H. Takahashi and K. Fujimoto

“Complex Plane Analysis for the Electrochemical Studies”,

Ed. A. Kozawa, T. Hirai and M. Nagayama,

The U. S. Office of the Japanese

Electrochemical Society

Complex plane analysis on the impedance measurement has been reviewed for the oxide-covered metal electrode.

The analysis was applied for aluminium electrode coated with anodic oxide films to establish the chemical composition of the oxide film.

**Hydration of Barrier Type Anodic Oxide Films on Al  
in Water and Its Inhibition by Chromate**

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

Bulletin of the Faculty of Engineering Hokkaido  
University, No. 102, 103 (1981)

Compact oxide films were formed on Al in a neutral borate solution (pH 7.4, 20°C) by applying a constant potential of 50 V (vs. SCE), and then they were immersed in twice distilled water or a 0.001 mol/dm<sup>3</sup> chromate solution (pH 7.0). The composition changes in the oxide films before and after immersion were examined by X-ray photoelectron spectroscopy (XPS) and chemical analysis, combined with chemical sectioning of the films in a sulfuric acid solution. After a 3 day immersion in distilled water the outer part of the film contained a three fold number of OH<sup>-</sup> ions as before immersion, and the film retained only 30 V instead of 50 V. The concentration profile of electrolyte anion (BO<sub>2</sub><sup>-</sup>) in the film remained unchanged, showing that the deterioration of the film is not due to dissolution and reprecipitation but is caused by hydration of the oxide. It was found that the hydration is strongly inhibited by the presence of chromate. XPS and chemical analysis showed that CrO<sub>4</sub><sup>2-</sup> ions are adsorbed on the oxide surface to form a monolayer, thus hindering the penetration of water molecules into the oxide layer. (Japanese)

## Electrochemical Measurements of Zinc Phosphate Solution

C. -G. Kin, T. Ohtsuka and N. Sato

Bulletin of the Faculty of Engineering, Hokkaido  
University, No. 104, 57 (1981)

Measurements of pH and electrochemical potential of zincphosphating solutions were made in a temperature range from 25°C to 85°C for the purpose of establishing a monitoring technique of the solution property. Platinum electrodes are applicable for the measurement of the potential of the redox system in the solution even at 85°C and can detect the difference in the redox potential of the solution at different stages of the zinc-phosphating operation. The solution pH, measured with a glass electrode for high temperature, remains constant at a value of about 2.3 at 85°C during the operation. It is also found that the potentials of iron and zinc electrodes change with time corresponding to the growth of zinc phosphate film. From the potential change of iron electrodes it is suggested that the film formation is completed within 3 minutes at 85°C in the zinc phosphate solution for industrial use. (Japanese)

**Benzotriazole and Tolyltriazole as Corrosion  
Inhibitors for Copper and Brasses**

T. Notoya and G. W. Poling

Corrosion Engineering (Boshoku Gijutsu)

30, No. 7, 381 (1981)

The Influence of Benzotriazole (BTA) and Tolyltriazole (TTA) as corrosion inhibitors for copper and brasses in 3% NaCl solutions have been investigated using infrared reflection-absorption spectroscopy, electrochemical polarization, corrosion tests and scanning electron microscopy. The protection afforded by pretreatment was tested in chloride solutions in the presence and absence of BTA and/or TTA. TTA by itself was found to be equally as effective as BTA. Combination of BTA and TTA resulted in significant improvement in the protection of these metals, particularly in acidic solutions. Contrary to BTA, TTA appeared to be an adsorption-type inhibitor for copper and brass. (English)

## Corrosion Inhibitive Action of Benzotriazole and Its Derivatives

T. Notoya

Corrosion Inhibitor Seminar Text, Japan Association  
of Corrosion Control, May (1981)

This text describes a chronological review of corrosion inhibition mechanisms of benzotriazole and its derivatives mainly for copper and copper alloys. The role of underlying oxide films present on the metal surface is stressed in inhibition mechanisms of the inhibitors. It is believed that the protective action of benzotriazole and its derivatives is attributed to the formation of a semipermeable polymeric Cu-benzotriazolate film on the metal surface. Typical protective films formed on copper by benzotriazole can be described as multilayers, such as Cu/Cu<sub>2</sub>O/ thin Cu<sup>I</sup>BTA/ thick Cu<sup>I</sup>BTA (up to 5000 Å). It is suggested that the inner and highly protective Cu<sup>I</sup>BTA film is formed directly on the metal surface by "discharge-nucleation mechanism", while the outer and thick Cu<sup>I</sup>BTA film is formed by "dissolution-precipitation mechanism". The physico-chemical data on benzotriazole, tolyltriazole and benzotriazole carboxylic acid and the practical application performance of the inhibitors are also summarized. (Japanese)

**Inhibition and Acceleration Action of Benzotriazole  
and Its Derivatives to Zinc Corrosion**

T. Notoya and T. Ishikawa

Denki Kagaku **49**, No. 6, 369 (1981)

Effect of benzotriazole (BTA), Tolyltriazole (TTA) and benzotriazole carboxylic acid (BTA-COOH) on the corrosion of zinc in chloride solutions was investigated by gravimetry and visible-ultraviolet spectroscopy. These organic compounds are widely used and most effective corrosion inhibitors for copper and its alloys. The BTA and its derivatives are shown to be good inhibitors for zinc in neutral chloride solutions. The inhibition efficiency of the three compounds was in the order of  $BTA < BTA-COOH < TTA$ . In the acidic chloride solutions (pH less than 2), however, all of the compounds accelerate dissolution of zinc producing red-soluble metal complexes. The degree of acceleration was in the order of  $BTA-COOH < TTA < BTA$ . (Japanese)

**Corrosion of Aluminum Copper Alloy and Inhibition Action  
of Benzotriazole, Tolyltriazole and Hydroquinone  
in Sodium Hydroxide Solutions**

T. Notoya and T. Ishikawa

Bulletin of the Faculty of Engineering, Hokkaido  
University, No. 105, 1 (1981)

The corrosion rates of an aluminum-copper alloy (2024, Super Duralumin) in sodium hydroxide solutions of seven different concentrations were determined gravimetrically at 30°C. The influence of three organic compounds, hydroquinone (HQ), benzotriazole (BTA) and Tolyltriazole (TTA), on the corrosion behavior of the aluminum-copper alloy was investigated in a concentration range from 0.01 to 0.1 mol/l of sodium hydroxide solutions. The corrosion of the alloy was found to be strongly dependent on the pH level of the alkaline solutions, and additions of these compounds resulted in a decrease of pH of the solution and thus leading to the decrease of its corrosion rates. The corrosion tests using a solution of constant pH (=12.8) showed that the inhibition efficiency increased with the increasing concentration of the compounds and the maximum inhibition efficiencies of HQ, BTA and TTA at a concentration of 0.1 mol/l were 40, 13 and 16%, respectively in 0.1 N NaOH solutions. The inhibition mechanism was discussed in relation to the nature of the corrosion product layer formed on the metal surface. (English)

**Sulfidation Properties of an Fe-25Cr Alloys  
in H<sub>2</sub>S-H<sub>2</sub> Atmospheres**

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

Report of J. S. P. S. **22**, No. 3, 405-418 (1981)

Sulfidation properties of an Fe-25Cr alloy were investigated over the large extent of sulfur partial pressures in H<sub>2</sub>S-H<sub>2</sub> atmospheres at temperatures of 700, 800 and 900°C by making use of TGM, X-RAY diffraction, O. M., SEM and EPMA.

Parabolic growth of the sulfide scale were observed after brief incubation periods. The parabolic rate constants obtained were in the range  $10^{-11}$  to  $10^{-5}$  g<sup>2</sup>/cm<sup>4</sup>sec. Sulfidation behavior of this Fe-25Cr alloy could be divided into three regions depending on sulfur pressure, that is, at 700°C region (I)  $<P(S_2)=10^{-10}$  atm,  $P(S_2)=10^{-10}<$  region (II)  $<P(S_2)=10^{-7}$ , and  $P(S_2)=10^{-7}<$  region (III). These critical sulfur pressures of  $10^{-10}$  and  $10^{-7}$  atm shifted toward higher sulfur pressures at high temperatures. The sulfidation rate in the region (I) was extremely low due to the sole formation of chromium sulfide containing a small amount of iron, where upon the sulfidation rate abruptly increased between region (I) and (II). This rate increased monotonically with sulfur pressure in region (II) but it tended to reduce in the region (III) above the critical sulfur pressure. This sulfidation behavior is ascribed to the changes in the scale structures from a single layer with solid solution of FeS and CrS<sub>x</sub> in region (II) to duplex-layers of FeS and CrS<sub>x</sub> phases in region (III). (Japanese)



## High-Temperature Sulfidation of Iron and Steels

K. Nishida

Corrosion Engineering (Boshoku Gijutsu)  
30, No. 7, 409-420 (1981)

High-temperature sulfidation of iron and steels does not seem so popular as oxidation of these alloys. Nevertheless, the sulfidation of steels is very important in the current industries. The article gives an outline on the corrosion kinetics and scale morphologies during sulfidation of iron based binary and ternary alloys as well as pure iron.

Especially, the sulfidation of some alloys is mentioned in low sulfur pressures. (Japanese)

## The High Temperature Corrosion of Iron in SO<sub>2</sub> Atmospheres

K. Kurokawa, T. Narita and K. Nishida  
Corrosion Engineering (Boshoku Gijutsu)  
30, No. 7, 396-403 (1981)

The scaling kinetics of iron in the argon-diluted sulfur dioxide gas atmospheres were investigated by thermogravimetry at 1073 K in SO<sub>2</sub> partial pressures from 20 to 10<sup>5</sup> Pa; the reacted specimens were characterized by means of metallography, X-ray diffractometry, and electron microprobe analysis. The scaling kinetics varied with corrosion time, that is, (1) from linear to primary parabolic (below 10<sup>3</sup> Pa), (2) from primary parabolic to secondary parabolic (between 10<sup>3</sup> and 10<sup>4</sup> Pa), and (3) only secondary parabolic (above 10<sup>4</sup> Pa) rate laws. The morphology of scales formed in the SO<sub>2</sub> partial pressures lower than 10<sup>4</sup> Pa showed the lamellar structure consisting of oxide and sulfide, which was produced in linear and primary parabolic periods, and in the secondary parabolic period the oxide was mainly produced. In high SO<sub>2</sub> partial pressures (above 10<sup>4</sup> Pa), the scales were composed of the oxides of wüstite and magnetite phases, though the mixture of wüstite and ferrous sulfide was observed in the vicinity of the metal/scale interface. The platinum marker located on the metal surface was found always just on the metal surface during corrosion over the whole range of SO<sub>2</sub> partial pressures. The linear rate constant was proportional to about 0.63 power of SO<sub>2</sub> partial pressure. The kinetics in the linear period was discussed from the observed linear rate constant and calculated mass fluxes of SO<sub>2</sub>, O<sub>2</sub> and S<sub>2</sub> molecules in the gas atmosphere. Thus, the dissociation process of the adsorbed O<sub>2</sub> and S<sub>2</sub> molecules produced on the scale surface was concluded to be the rate determining step in the linear period. (Japanese)

**Morphology of Scales Formed on Some Fe-Mn  
Alloys under Low Sulfur Pressures  
at High Temperature**

K. Nishida and T. Narita

Proceedings of 8th ICMC, 821 (1981)

Some Fe-Mn alloys containing about 12, 29 and 48 mass% Mn were sulfidized in sulfur pressures of  $10^3 \sim 10^{-6}$  Pa and then examined by TGM, EPMA, SEM, and X-ray diffraction. With respect to the kinetics and scale morphologies, sulfidation behaviors could be divided into three pressure ranges, that is, region I  $> P(S_2) = 10^{-2}$  Pa,  $P(S_2) = 10^{-4} <$  region II  $< P(S_2) = 10^{-2}$  Pa, and region III  $< P(S_2) = 10^{-4}$  Pa for the 12% alloy at 1073 K. A steep decrement of parabolic rate constants was observed in region II at each temperature for all alloys, and ascribed to the change in the scale structure from the duplex (Mn, Fe)S and (Fe, Mn)S layers to the single (Mn, Fe)S layer. The latter scale accompanied with extensive internal sulfidation. (English)

**Continuous Measurement of Corrosion Rate and  
Corrosion Loss in Molten Salt Systems**

T. Ishikawa and T. Sasaki

Proc. the 8th International Congress on Metallic  
Corrosion, Vol. 1, pp. 803-808 (1981)

In order to elucidate corrosion behavior and amount of corrosion in various molten salts, usual immersion tests were carried out and also electrical resistance of wire specimens were followed with time in ammonium bisulfate melts of 170° to 230°C and in alkali nitrate melts of 350° to 450°C. According to time variation of measuring resistance, amounts of corrosion and corresponding rate constants can be calculated from diameter, length, specific resistance and density of the specimens without results of immersion tests. Corrosion behaviors clarified are as follows: 1) Linear law for iron in bisulfate melts, 2) Logarithmic law for stainless steel in the same melts, 3) Parabolic law for iron in nitrate melts. Although limiting by shape and size of the specimen, such sensitive resistometry would be an useful technique for continuous determination of corrosion behavior in various salt systems. (English)

**New Application of Auger Electron Spectroscopy  
(SAM and A ES-SIMS)**

M. Seo

Bull. Japan Inst. Met., **20**, No. 7, 586 (1981)

This article described new application of Auger Electron Spectroscopy (AES) in the field of surface science and surface technology. The usability of Scanning Auger Microprobe (SAM) developed for microanalysis of solid surface was discussed in relation to the problem of quantitative analysis. Furthermore, it was emphasized that the combination of AES with Secondary Ion Mass Spectroscopy (SIMS) was powerful for the measurement of depth composition profile and for the adsorption layer analysis. (Japanese)

## Photoelectric Polarization Methods

N. Sato

Bull. Japan Inst. Met., **20**, No. 7, 637 (1981)

This review paper describes the technique of photoelectric polarization recently developed in the field of electrochemistry and its application to the study of metallic corrosion. 1) Principles of photoelectric polarization. 2) Measuring methods. 3) Theories of photoelectric polarization of semiconductor electrodes. 4) Application of photoelectric polarization methods for the study of anodic oxide films formed on metals. (Japanese)

**Multiple-Angle-of-Incidence Ellipsometry**

T. Ohtsuka

Bull. Japan Inst. Met., **20**, No. 7, 614 (1981)

Ellipsometric measurement at multiple angles of incidence is effective in the study of surface film on metal or semiconductor. The measurement results of anodic oxide films on Mo and of oxide films of the coloured stainless steel have been reported as examples. With the aid of a suitable computation program, the optical constants of the surface film and substrate metal or semiconductor in addition to the film thickness are simultaneously determined. (Japanese)

**A Mössbauer Spectroscopic Study of Sulfidation  
of Iron-Manganese Alloys**

K. Nishida, T. Tani, T. Narita and H. Ohashi  
Corrosion Science **21**, No. 9, 627-637 (1981)

Mössbauer absorption spectra were measured for sulphides obtained from iron-manganese alloys at 1000°C under  $3.5 \times 10^{-7}$ -1 atm. sulphur pressures. Depending on the sulphidation conditions, FeS<sub>2</sub>, Fe<sub>1-x</sub>S, stoichiometric FeS and MnS type sulphides were identified. For the Fe<sub>1-x</sub>S phase Fe(II) ions with and without first neighbour vacancies were distinguished. From the dependence of the isomer shift and the relative intensity of the absorption it was possible to construct a Maurer equilibrium diagram for the FeS-MnS quasi binary system. An explanation for the role of manganese in sulphidation resistance is also given. (English)



**X-ray Photoelectron Spectroscopy —Angular-resolved  
XPS, High Pressure XPS, and Other  
New Techniques—**

H. Konno and M. Nagayama

J. Japan Institute of Metals **20**, 586 (1981)

The construction of the apparatus, the principle of the methods, and the recent progress in the instrumentation and application are described. (Japanese).

**Paramagnetic Cobalt (III) Complexes with Organic  
Ligands. VI. An X-Ray Photoelectron  
Spectroscopic Study**

T. Yamamoto, M. Mori and H. Konno  
Bull. Chem. Soc. Japan, **54**, 1995 (1981)

Paramagnetic tetraammine-5-nitrosalicylato cobalt complex, paramagnetic  $\mu$ -hyperoxo-dicobalt complexes and related diamagnetic compounds have been studied by X-ray photoelectron spectroscopy. In all these compounds, the binding energies of Co 2p electrons and their spin-orbit separation were those of usual Co (III) complexes. In the spectrum of paramagnetic tetraammine-5-nitrosalicylatocobalt salt, satellites appeared near the Co 2p peaks showing certain spin density at the cobalt atoms. At the same time, the C 1s spectrum showed that considerable portion of carbon atoms has high binding energy suggesting delocalization of electron hole over the organic ligand. The O 1s peaks in  $\mu$ -hyperoxo complexes were ca. 0.6 eV higher than those in  $\mu$ -peroxo complexes. Deconvolution of the O 1s peak in the  $\mu$ -OOH complex gave OH, =O-, and H<sub>2</sub>O peaks at the 1:1:1 ratio, supporting the  $\mu$ -OOH formulation. (English)

## Application of STEM-EDX System to Metals and Alloys

T. Takeyama, H. Takahashi, S. Ohnuki,  
Y. Sato and S. Mochizuki

Hitachi Instrument News, Electron Microscopy  
Edition, No. 8 (1981) p. 4-8.

Scanning transmission electron microscopy of 200 kV (STEM) and energy dispersive X-ray microanalysis were applied to study the transformation of  $\gamma$  to  $\alpha'$  and microsegregation caused by electron irradiation.

Microstructure of ferritic Fe-Ni alloy consisted of dark and bright images by STEM. Dark area had higher concentration of Ni, and identified as  $\alpha'$  martensite formed though the transformation of  $\gamma$  phase. From DEX analysis of irradiated Cu alloys, the enrichment or depletion of solute atoms were detected on grain boundaries and voids. The result indicates that irradiation defects interact with solute atoms to cause the microsegregation on the defect sinks.

## ABSTRACTS

### **A Study of the Point-Defect Mobility in Ag-Cu by High-Voltage Electron Microscopy**

H. Takahashi and K. Urban

Phys. stat. Sol. (a) **67**, (1981) p. 347

A study is carried out by high-voltage electron microscopy on the relative mobility of interstitials and vacancies in an Ag-0.17 at%Cu alloy in the temperature range of 300 to 775 K. Shortly after starting the irradiation stacking-fault tetrahedra are formed in the whole range of temperatures investigated. This indicates that the mobility of vacancies is higher than that of self-interstitials. This can be explained by the formation of interstitial-solute complexes retarding interstitial motion. During further irradiation solute segregation occurs to point-defect sinks with the result that the interstitial mobility increases to the extent that it eventually surpasses that of the vacancies.

**The Effect of Irradiation and Post-Irradiation Annealing  
on the Yield Stress and Microstructure  
of Vanadium-Carbon Alloys**

H. Takahashi, S. Ohnuki and T. Takeyama  
Journal of Nuclear Materials 96 (1981) 233

Vanadium and vanadium-carbon alloys containing 0.15, 0.3 and 1 at% carbon were irradiated in JMTR with fast neutrons ( $E_n > 1$  MeV) at 773 K to a dose of  $5 \times 10^{24}$  n/m<sup>2</sup>. Tensile test and microstructural observations were carried out after irradiation and post-irradiation annealing. All of the specimens showed radiation hardening. The irradiation produced voids, dislocations and radiation-induced quasi-carbides, which were formed by the agglomeration of vacancies and carbon atoms. The radiation anneal hardening in the alloys occurred at 873 K. The void number densities in the alloys had a peak at 873 K while the quasi-carbides decomposed at the same temperature. Therefore, invisible voids existing in the as-irradiated condition would grow by absorbing the vacancies, which were released in the process of decomposition of the quasi-carbides during annealing, and the increase of the visible voids would effectively contribute to the radiation anneal hardening of these alloys.

## Carbon Segregation Around Voids in C<sup>+</sup> Ion-Irradiated Iron

H. Takahashi, T. Takeyama, S. Nakahigashi  
and T. Terasawa

Journal of Nuclear Materials 98 (1981) 227

The irradiation was performed for pure iron of about 99.996 wt% purity with 200 keV C<sup>+</sup> ions in the temperature range of 698 to 948 K at doses between 15 and 118 dpa. Void nucleation was detected uniformly throughout the irradiated area above 748 K, but void denudation with about 40 nm at 798 K, was formed in the vicinity of surface, and voids were distributed in the region from 40 to 200 nm. Most of the voids were truncated on (100) planes and void number density increased with increase in dose. Further more, very small precipitates were formed near the voids in the temperature range where a number of voids were nucleated. That is, a preferential segregation of the injected carbon atoms occurred around voids, indicating that a binding effect between a carbon atom and a vacancy is still operative, and that the segregation can be caused by a small dragging effect of carbon atoms with vacancy flow toward its sink sites. From identification of diffraction pattern of these precipitates, it was clarified that the precipitates were not graphite but cementite.

## Void Swelling and Segregation of Solute in Ion-Irradiated Ferritic Steels

S. Ohnuki, H. Takahashi  
and T. Takeyama

Journal of Nuclear Materials 103 & 104 (1981) 1121

Void formation and radiation induced segregation were investigated through the interaction between defects and solute atoms in pure iron, Fe-13 wt%Cr and Si or Ti doped alloys by 200 keV C<sup>+</sup> ion irradiation up to 118 dpa at 798 K. Microstructural observation was carried out by transmission electron microscopy, energy dispersive X-ray microanalysis and electron energy loss spectroscopy. The ferritic alloys exhibited significant resistance to void swelling. In Fe-Cr and Fe-Cr-Si alloys, the irradiation produced the precipitates consisting chiefly of chromium and implanted carbon, and chromium was enriched at grain boundaries and voids. In the Fe-Cr-Ti alloy, Ti-rich precipitates were formed, and chromium was depleted from grain boundaries. These facts suggest that the solute atom-defect interaction which controls void formation and segregation is affected by the presence of chromium and other alloying elements.

**Radiation-Induced Segregation at Internal Sinks in  
Electron Irradiation Binary Alloys**

H. Takahashi, S. Ohnuki  
and T. Takeyama

Journal of Nuclear Materials 103 & 104 (1981) 1415

Radiation-induced segregation phenomena in copper, nickel and iron based binary alloys were studied by means of a high voltage electron microscope and an energy dispersive X-ray microanalyzer. The segregation was caused during electron irradiation of under-saturated Cu-2 at% Ni alloy. In supersaturated Cu-2 at% Ag and Cu-2 at% Fe alloys precipitates were formed near surfaces and grain boundaries in the early stage of irradiation, subsequently voids nucleated at the central region of foil. On the other hand, alloying elements were depleted at defect sinks in Ni-2 at% Cu, Fe-5, 13 at% Cr and Fe-1 at% Mn alloys. The changes of solute concentration near sinks in these alloys indicate that the size effects lead to the segregation or depletion and under- and over-size solutes tend to migrate toward and away from the sinks, respectively.



## Effect of Neutron and Electron Irradiation on Low Manganese Steels

T. Takeyama, S. Ohnuki  
and H. Takahashi

Transactions ISIJ, Vol. 21 (1981) p. 326

The interaction between solute atoms and radiation induced defects was studied by means of tensile test and transmission electron microscopy. The defects were produced by neutron irradiation at 473 K to a fluence of  $6.4 \times 10^{22}$  n/m<sup>2</sup> ( $E_n > 1$  MeV) and electron irradiation at 650 kV electron microscope to a fluence of  $7 \times 10^{25}$  e/m<sup>2</sup>.

Radiation hardening and radiation embrittlement occurred by neutron irradiation. The yield stress increased and the total elongation decreased with the increase of manganese content. Dislocation loops were observed in the iron but not detected in manganese alloys. Therefore, it will be considered that the defects would be trapped by manganese atoms and then formed complexes with carbon. Defects produced by electron irradiation were not observed by electron microscopy in the manganese alloys, however, after annealing above 598 K the defect clusters, presumably interstitial type, appeared and grew. The annealing behaviors were similar for both the neutron and electron irradiated specimens.

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

**Study of Segregation in Alloys Irradiated  
by Ions and Electrons**

T. Takeyama, S. Ohnuki  
and S. Maruyama

Bulletin of the Faculty of Engineering, Hokkaido  
University, No. 104 (1981) p. 65

Radiation induced segregation on binary alloys, 316 stainless steel and ferritic alloys was studied by means of an energy dispersive X-ray microanalyzer attached to a 200 kV STEM. Irradiation was carried out in a 650 kV high voltage electron microscope up to 10 dpa for binary alloys and in 200 keV C<sup>+</sup> ion accelerator up to 57 dpa. The segregation was observed on internal sinks, such as grain boundaries, voids, dislocation loops and precipitates. Radiation induced precipitation was caused by the segregation in unsaturated alloys. The type of segregation or depletion depended primarily on the difference of the size factor. However, unexpected segregation was detected in some alloys irradiated by ions. The segregation and depletion of the solutes could be affected by the nucleation and growth of voids.

## Strengthening of Cast Iron Circular Plates by Annular Ribs

T. Noguchi and K. Nagaoka

IMONO, 53, (2), 73 (1981)

The bending strength of cast iron circular plates with annular ribs was evaluated for various dimensions and locations of the ribs. In view of the non-elastic behavior of cast iron, strength analysis was carried out using the finite element method for the calculation of stress distribution in the plate, and using the stress boundary layer  $\delta$  as fracture criterion as proposed by the authors in earlier report. Results were well verified experimentally.

An annular rib is most effective when its distance from the center is 0.3 to 0.4 of the plate radius, where the strength is increased by more than 50% with an increase of only 8% of the casting weight. If a rib is nearer to the center than the above distance, it is less effective, because it can cause fracture at the top or outer fillet of the rib. Tapered plates are superior to plates with ribs in terms of the ratio of strength to weight increase. An advantage of castings is that the structural strength can be increased easily by appropriate design of ribs and wall thickness. (Japanese)

## **Research on Strength Characteristics of Cast Iron and Its Evaluation**

T. Noguchi

Doctoral Thesis (Hokkaido Univ.) June 1981

In evaluating the strength of structural components made of cast iron, there are often large differences between the strength calculated by design formulas and that measured by fracturing tests. Such differences are especially remarkable in the strength of bending and notched members. In this paper, a new method is proposed for evaluating strength of components under wide range of nonuniform stresses.

The author induced the new method of strength evaluation from analysis of nonelastic behavior of cast iron with elasto-plastic stress calculation by FEM and a fracture criterion based on a depth in which the stress exceeds the tensile strength of the iron. The critical value of the overstressed depth is related metallurgically to the size of eutectic graphite cells in the iron.

The criterion of strength evaluation is applied to not only beams and notched bars but also T-beams and circular plates with various dimensions.

Contents; Microstructures and Mechanical Behaviors of Cast Iron./Bending Strength./Strength of Notched Members./Fracture Criterion and Over Stressed Depth./Strength Evaluation of Cast Iron Components. (Japanese)

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

Y. Suzuki, S. Sayama and K. Nishida

Transactions of The Iron and Steel Institute  
of Japan **21**, No. 1, 32-39 (1981)

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)

## Interdiffusion in the $\alpha$ -Solid Solution of the Fe-Sn System

T. Yamamoto, T. Takashima and K. Nishida

Journal of the Japan Institute of Metals

45, No. 10, 985-990 (1981)

For the purpose of studying interdiffusion in the  $\alpha$ -solid solution of the Fe-Sn system, experiments were performed using the method of vapor-solid couple at temperatures between 1073 and 1373 K. As a vapor source, fine powder of a 40 mass% (23.9 at%) Sn-Fe alloy was used. The surface concentration of Sn in diffusion-annealed test pieces almost coincided with the solubility limits reported in the Fe-Sn phase diagram at 1173-1373 K, while significant deviations in the solubility limits were found at 1073 K and 1123 K. Fine alumina markers placed on the test pieces prior to diffusion remained on the surface after annealing. Each penetration curve at temperatures between 1073 and 1173 K was similar to the error function curve for a particular  $\tilde{D}$  value.

The value of  $\tilde{D}$  showed a relatively small dependence upon the Sn concentration at each temperature. The activation energies for interdiffusion,  $\tilde{Q}$ , decreased from 228 to 221 kJ/mol with increasing Sn concentration. The impurity diffusion coefficients of Sn in Fe,  $D_{\text{Sn}}^*$ , between 1073 and 1173 K were obtained from extrapolation of  $\tilde{D}$  to 0 at %Sn and its activation energy,  $Q_{\text{Sn}}^*$ , was evaluated to be 229 kJ/mol. The relationship between the entropy term,  $\tilde{D}_0$ , and  $\tilde{Q}$  is represented by the following equation:

$$\ln(\tilde{D}_0/\text{m}^2 \cdot \text{s}^{-1}) = 6.5 \times 10^{-5} (\tilde{Q}/\text{J} \cdot \text{mol}^{-1}) - 22.4. \quad (\text{Japanese})$$

## Reaction of Silver, Calcium, and Iron Sulfides with Steam

R. Shibayama and T. Tanaka

Transactions of the Japan Institute of Metals,  
Vol. 22, No. 6 (1981), pp. 385 to 391

Reactions between steam and metal sulfides such as  $\text{Ag}_2\text{S}$ ,  $\text{CaS}$ , and ferrous sulfide were investigated in the temperature range 900–1100 K by monitoring the evolved hydrogen. These reactions are characterized by solid products and can be classified into three types, that is, metal, oxide, and sulfate, respectively. For the reaction of  $\text{CaS}$  or  $\text{Ag}_2\text{S}$  with steam, it was concluded that generation of  $\text{H}_2$  is due to the oxidation of  $\text{S}^{2-}$  in the sulfide phase. In ferrous sulfide, the contribution of the oxidation of  $\text{Fe}^{2+}$  to the hydrogen evolution is of importance. Furthermore, it was confirmed that selective oxidation of  $\text{Fe}^{2+}$  to the hydrogen evolution is of importance. Furthermore, it was confirmed that selective oxidation of  $\text{Fe}^{2+}$  or  $\text{S}^{2-}$  in the ferrous sulfide proceeds depending upon the extent of nonstoichiometry of ferrous sulfide. It is also shown that the addition of lime to ferrous sulfide results in a considerable increase in hydrogen concentration. (English)

## Hydrogen Reduction of Lead Sulfide

H. Kiuchi and T. Tanaka

Journal of the Mining and Metallurgical

Institute of Japan, 97, 113 (1981)

Reduction rate of PbS with H<sub>2</sub> was measured thermogravimetrically in the temperature range 380° to 750°C by using thin disks prepared from synthetic and natural PbS powder.

The reduction rate of synthetic PbS was about twice that of galena below 450°C, whereas above 650°C no difference was detected in their rates. The rate decreased when a sample was covered with the formed metallic Pb at 550°C, but the tendency was not observed at 710°C. The measured rates surpassed the vaporization rates of PbS significantly and the Arrhenius plot yielded two straight lines. The activation energies were determined to be 15 kcal/mol below 450°C and 33 kcal/mol above 650°C respectively.

It can be presumed from these results that the reduction in the lower temperature range is governed by a mechanism different from that in the higher temperature. At temperatures below 450°C, the experimental results suggest that the rate is chemically-controlled by the heterogeneous reaction between H<sub>2</sub> and solid PbS. Absolute reaction rate theory was used to develop an analytical expression for this heterogeneous reaction. The rate constants calculated with the equation assuming that the surface of PbS is sparsely covered by adsorbed hydrogen agreed favorably with the experimental data.

On the other hand, above 650°C, it can be suggested that homogeneous reaction between gaseous PbS and H<sub>2</sub> is dominant and the reaction proceeds not at the surface or in the bulk stream of H<sub>2</sub>, but in the boundary gas layer and enhances vaporization of PbS. The model can be supported by the following observations : (1) The surface of the reduced PbS at high temperature shows a similar structure to the surface which is allowed to evaporate under reduced pressure. (2) Reduction rate is independent on the



size of the grains which comprise of a sample disk and also on the much adhesion of metallic Pb on the surface. (3) Serious difference in the activation energies in the reduction and vaporization. (Japanese)

**Some Aspects on Porous Properties of Iron Oxides  
Containing Foreign Oxides Reduced  
by Hydrogen**

Y. Suzuki, M. Yamamoto, T. Kotanigawa  
and K. Nishida

Metallurgical Transactions B 12B,  
No. 12, 691-697 (1981)

The objective of this study is to prepare suitable iron ores for industrial reduction processes. Therefore, the properties of porous, green and indurated hematite compacts as well as iron ore were investigated by quantitatively measuring pore volume, BET surface area and pore size distribution. Furthermore, the influence of foreign oxides on porous properties was investigated. Based on these data, the mechanism of sintering process of the compacts was discussed. The results obtained here suggest that the porosity of the compacts after almost 100 pct reduction does not depend upon whether the compacts were indurated or not. Therefore, it would be concluded that indurating the compact is not necessary for pulverized iron ores containing foreign oxides when reduced in the process such as a fluidized bed system. (English)

**Expansion and Contraction during Hydrogen Reduction  
of Green and Pre-heated Hematite Compacts  
Containing Foreign Oxides**

Y. Suzuki, S. Sayama and K. Nishida

Transactions of The Iron and Steel Institute  
of Japan **21**, No. 12, 870-878 (1981)

Effects of the addition of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  to green and pre-heated hematite compacts on the expansion/contraction of the two compacts when reduced in a hydrogen atmosphere were studied by measuring changes in the electrical resistance and thermal expansion/contraction.

The results obtained are as follows :

(1) Green compacts are reduced faster than pre-heated compacts. The reduction of green compacts proceeds simultaneously at the inner parts as well as at the surfaces, while pre-heated compacts are reduced slowly in accordance with the core model where the reduction proceeds gradually from the outer to the inner parts.

(2) In case of green compacts, the smaller the oxide particle size is, the slower the reduction rate is and also the less the shrinkage due to reduction is.

(3) Cracking of green and pre-heated compacts containing foreign oxides is considered to be due mainly to the local stresses in compact matrix caused by the difference in shrinkage between the contained oxides of different sizes and, in some cases, to the so-called phase-separated structure.

(4) The electrical resistance is clearly related to expansion/contraction over 95% reduction in case of green compacts except the compact containing  $\gamma$ -alumina ; in case of pre-heated compacts, over 90% reduction when silica is contained and over about 60% reduction when alumina is contained. (English)

**Removal of Arsenic from the Hot Waste Water from  
Geothermal Power Plants by Means of Ion  
Exchange Technique with a Closed  
Desorption System**

T. Nagai and R. Togashi

Reports of the Asahi Glass Foundation for Industrial  
Technology, Vol. 38, p. 1 (1981)

Removal of arsenic by means of ion-exchange technique was studied for the hot waste water from geothermal power plants. This involved the development of a porous-type ionexchanger which was made by means of in-situ precipitation of zirconium hydroxide in some porous carrier, followed by drying in order to fix the precipitates upon the wall of the micropores in the carrier.

The exchangers thus made showed rapid adsorption rates for arsenic in hot water, whereas the commercial exchangers of gel-type were insufficient in kinetic abilities. As the porous-type ion-exchanger contains small amount of zirconium per unit volume, it aims at lowering its manufacturing cost down, hence resulting in the feasible treatment of the hot waste water.

In order to avoid the accumulation of the detrimental materials resulted from the ionexchange operations, a closed system for the eluate by means of manufacturing pure arsenic oxide by the Freeze-Melt process was developed. (Japanese)

## Mechanism of Hydrogen Evolution Reaction on Gold in Aqueous Sulfuric Acid and Sodium Hydroxide

T. Sasaki and A. Matsuda

J. Res. Ins. Catalysis, Hokkaido Univ.,  
29, 113 (1981)

The hydrogen overvoltage on gold has been splitted into the components  $\eta_1$  and  $\eta_2$  which are caused respectively by the change of the free charge and the intermediate species on the electrode surface by the galvanostatic transient method in aqueous sulfuric acid and sodium hydroxide. It has been found that  $\eta_1$  is responsible for the promotion of the rate of the electron transfer step which is the discharge of hydronium ion in acid and that of  $\text{Na}^+$  ion in alkaline solutions, and that the recombination of adsorbed hydrogen atoms is rate-determining at low current densities in acid. In alkaline solutions, however, there appears an overvoltage component due to the specific adsorption of some species other than the intermediate Na atom which may result in the irregular variation of the polarization curves of the overall reaction. (English)