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CONTENTS

Metals in Fused Salt :

Anodic Oxide :

Passive Films :

General Corrosion :

Stress Corrosion Cracking :

Straining Electrode :

Heat Transfer Corrosion :

Corrosion Rate Estimation :

Leaching of Pyrite :

Metal Oxide Dissolution :

Hydroxide Membrane :

Hydrogen Production:

Adsorption, Catalysis and Electron Emission:

Surface and Vacuum Technology:

Analysis with Electron Linear Accelerator:

ELECTROCHEMISTRY LABORATORY

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Passivity of iron-group metals and alloys in aqueous solutions is being investigated in this laboratory. New information about the structure and composition of passive oxide films on iron, nickel, cobalt and chromium in solutions of pH ranging from acid to base has been collected by means of ellipsometry as well as electrochemical measurements. In addition, Auger electron spectroscopy is being used to analyse the composition of passive oxide films on iron and iron-base alloys. Also, in relation to the passivity study, development of a high sensitive-automatic ellipsometer and improvement of electrode impedance techniques are being made for the purpose of investigating the rapid change in thickness of the passive film during passivation or cathodic reduction of the film. Besides, an ellipsometric spectroscopy technique is being developed.

Furthermore, anionic and cationic transport properties of metal hydroxide membranes are being investigated with the aim of understanding the role of metal hydroxides that form during corrosion. There is also a fundamental study being carried out on fuel cell catalysis with hydrogen and hydrocarbon fuels in acid solutions by the use of platinum and some extremely corrosion-resistive, amorphous alloys as electrode.

Professor Sato attended the Japan-U.S. Seminar of "Passivity and Its Breakdown on Iron and Iron Base Alloys" held in Honolulu, Hawaii, U.S.A., and the 6th International Congress on Metallic Corrosion held in Sydney, Australia. Dr. Seo attended the Fall Meeting of the Electrochemical Society held in Dallas, Texas, U.S.A., and then visited the Professor Staehle's Laboratory at the Ohio State University for the international collaborative research on the passivity of iron-base alloys supported by JSPS in Japan and NSF in U.S.A.

Professor A. B. Wintebottom has come to this laboratory as a visiting professor and stayed for 3 months. Four other foreign scientists visited this laboratory: Professor J. Klerer (Division of Science and Mathematics, The Cooper Union for the Advancement of Science and Art, Cooper Square, N.Y., U.S.A.), Dr. B. Eremias (State Research Institute for Protection of Metals, Prague, Czechoslovakia), Dr. V. Ashworth (Center for Corrosion and Protection Studies, Institute of Science and Technology, University of Manchester, England) and Dr. J. E. Castle (Department of Metallurgy and Materials Technology, University of Surray, England).

Oral Presentations

Composition of Passive Oxide Films on Iron in Alkaline Solutions; R. Nishimura, K. Kudo and N. Sato: 10th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1975.

Structure of Trans-passive Oxide Films on Cobalt; T. Ohtsuka, K. Kudo and N. Sato: *ibid.*, Feb., 1975.

Passivity of Iron, Nickel and Cobalt —General Theory of Passivity—; N. Sato: Japan-U.S. Seminar of Passivity and Its Breakdown on Iron and Iron Base Alloys, Honolulu, Hawaii, U.S.A., March, 1975.

AES Analysis of Anodic Oxide Films on Iron and Nickel; M. Seo, J. B. Lumsden, R. W. Staehle and N. Sato: 42nd Annual Conference of the Japan Electrochemical Society, Apr., 1975.

Characteristics of Precipitated Nickel Hydroxide Membranes; M. Sakashita and N. Sato: *ibid.*, Apr., 1975.

AES Analysis of Passive Oxide Films on Iron; M. Seo, J. B.

Lumsden, R. W. Staehle and N. Sato : Spring Meeting of the Japan Institute of Metals, Apr., 1975.

AES Analysis of Iron Oxide Films and Chemical Shift ; M. Seo, J. B. Lumsden, R. W. Staehle and N. Sato : *ibid.*, Apr., 1975.

Ellipsometry of Passive Oxide Films on Fe–Ni Alloys ; K. Kudo : *ibid.*, Apr., 1975.

On the Passivity of Iron ; N. Sato ; *ibid.*, Apr., 1975.

AES Analysis of Surface Oxide Films on Iron; M. Seo : Tohoku Section Meeting of the Japan Society for Analytical Chemistry, Apr., 1975.

AES Analysis of Surface Oxide Films on Iron, Nickel and Fe–Ni Alloys ; M. Seo, J. B. Lumsden, R. W. Staehle and N. Sato : 2nd Annual Conference of the Japan Society of Corrosion Engineering, May, 1975.

Dissolution of Hydrous Metal Oxides in Acid Solutions ; M. Seo and N. Sato ; *ibid.*, May, 1975.

Passive Conditions of Iron, Cobalt and Nickel ; N. Sato : *ibid* May, 1975.

Electrode Impedance of Passivated Iron Group Metals ; K. Kudo, N. Arayama and N. Sato : *ibid.*, May, 1975.

Selective Ion Permeability of Precipitated Nickel Chromate, Molybdate and Tungstate Membranes ; M. Sakashita, N. Sato : *ibid.*, May, 1975.

Exo-electron Emission and Ellipsometry as a Surface Research Method ; N. Sato : Hokkaido Section Meeting of the Japan Chemical Society and the Japan Catalysis Society, Sept., 1976.

Surface Electronic Structure of Iron Oxides Estimated from Chemical Shift of Auger Electron; M. Seo and N. Sato: Fall Meeting of the Japan Institute of Metals, Oct., 1975.

Diffusion Potential of Precipitated Hydroxide Film as a Corrosion Product ; M. Sakashita and N. Sato : *ibid.*, Oct., 1975.

Composition of Passive Oxide Films on Iron in Acid Solutions ; R. Nishimura, K. Kudo and N. Sato : *ibid.*, Oct., 1975.

Ellipsometry of Passive Oxide Films on Chromium in Neutral Solutions ; R. Saito, K. Kudo and N. Sato : *ibid.*, Oct., 1975.

Anodic Oxide Films on Cobalt in Oxygen Evolution Region; T. Ohtsuka, K. Kudo and N. Sato: *ibid.*, Oct., 1975.

Anodic Oxidation of Cobalt in Acid Solutions; T. Ohtsuka, K. Kudo and N. Sato: *ibid.*, Oct., 1975.

On Induction Time of Pit Generation; N. Sato, T. Nakagawa, K. Kudo and M. Sakashita: 22nd Symposium of the Japan Society of Corrosion Engineering, Oct., 1975.

The Passive Films on Iron in Neutral Solutions; N. Sato, K. Kudo and R. Nishimura: 6th International Congress on Metallic Corrosion, Dec., 1975.

On Potential Distribution at Metal Oxide/Solution Interface; M. Seo and N. Sato: Hokkaido Section Meeting of the Japan Electrochemical Society, Dec., 1975.

AES Analysis of Boron in Passive Oxide Films on Iron in Boric-Borate Solutions; M. Seo, J. B. Lumsden, R. W. Staehle and N. Sato: *ibid.*, Dec., 1975.

HIGH TEMPFRATURE METAL CHEMISTRY LABORATORY

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

Students

J. Fujino, K. Kimura, S. Murai, H. Kinoshita, M. Takahashi,
K. Taniguchi, K. Aota, S. Araike, T. Matsunaga,
T. Nakajima, M. Yamada and M. Murakami

The laboratory is investigating the dry corrosion (oxidation and sulfurization) of metals and alloys. The diffusion in metals and oxides is also being investigated by means of solid couple and metallic vapor techniques on the basis of corrosion and protection researches. Furthermore, decomposition of metal carbides in a wet atmosphere is also being studied. The usage of a light beam furnace (L. B. F.) is casting a light on the new fields of research in the laboratory as a high temperature source (about 3000°C).

At present the research is being carried out on the followings:

(1) Oxidation of Co-based Ni and Fe alloys; The effect of the oxygen pressure on oxidation rates was further investigated to other kinds of Co-based alloys and the composition profile in the oxide solid solutions, (Co, Me)O, was obtained. Some modifications of the original theory were made in order that the calculated profile agreed very well with the observed one.

(2) The metallizing of refractory metals and their oxidation behavior; Details of the calorizing of Ta metal and its oxidation behavior were much clarified and other metals such as Mo, Zr, and W were also calorized and their oxidation behaviors were investigated.

(3) Interdiffusion in Ni–Sb and Ni–Zn systems; Ni metal sheets were exposed to Sb and Zn vapors to obtain mutual diffusion coefficients in their intermediate phases as well as in an α phase.

Such a process will be developed to multilayered systems by using of metallizing and homogenization.

(4) Application and modification of a light beam furnace; Some devices were developed to use the apparatus for synthesis of metal calchogenides in the variable sulfur pressures. By use of a two-color pyrometer, which measures the precise temperature of the molten oxides mixtures as well as pure oxides, the cooling curve of $Ta_2O_5+Al_2O_3$ mixtures was obtained, from which some parts of the phase diagram were made clear.

Prof. Nishida was regrettably unable to attend the 6th ICMC in Australia owing to his desease. Prof. W. W. Smeltzer, Professor of Metallurgy and Materials Science in MacMaster University, Canada, visited our laboratory to discuss the common problems in dry corrosion on his way back home from the meeting in Australia.

Oral Presentations

Sulfurization of high Mn-Ferrous Alloys in Sulfur Vapor; T. Tani, T. Narita and K. Nishida: 10th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1975.

High-Temperature Sulfurization of Mn–Fe Alloys; T. Narita and K. Nishida: The Spring Meeting of the Japan Institute of Metals, April, 1975.

Effect of Oxygen Pressure on the Oxidation of A Co–0.45 wt % Ni Alloy; K. Kimura, T. Narita and K. Nishida: The Hokkaido Section Meeting of JIM and ISIJ, May, 1975.

Calorizing of some Refractory metals and Its Effect on High-Temperature Oxidation of Them; J. Fujino, T. Narita and K. Nishida: *ibid.*, May, 1975.

Recent Research on High-Temperature Oxidation and its Several Problems; K. Nishida and T. Narita: Seminar sponsored by the Hokkaido Section of JIM, July, 1975.

Calorizing of Some Refractory Metals and their Oxidation Behaviors; J. Fujino, T. Narita and K. Nishida: The Fall Meeting of Japan Institute of Metals, Oct., 1975.

Oxidation Resistance of Calorized Ta Sheets (II); M. Hachinohe and K. Nishida: *ibid.*, Oct., 1975.

Effect of Oxygen Pressure on High-Temperature Oxidation of Co-0.45 wt % Ni Alloy; K. Kimura, T. Narita and K. Nishida: *ibid.*, Oct., 1975.

Theoretical Analysis of Cation Distributions in the (Co, Ni)O Scales Formed on Co-Low Ni Alloys (II); T. Narita and K. Nishida: *ibid.*, Oct., 1975.

Interdiffusion in a α Solid Solution of A Ni–Sb System; S. Murai and K. Nishida: *ibid.*, Oct., 1975.

Hydrolysis of Mn–C–Fe and Mn–C–Cr Ternary Alloys; K. Atarashiya: *ibid.*, Oct., 1975.

Synthesis of Oxides of Some Refractory Metals by Using of A Light Beam Furnace; K. Taniguchi, T. Narita, M. Hachinohe and K. Nishida: The 2nd Meeting of Hokkaido Section of Japan Electrochemical Soc., Dec., 1975.

ELECTROMETALLURGY LABORATORY

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

Students

H. Ichikawa, M. Konno, O. Yamamoto, T. Abe, A. Suzuki,
A. Imai, S. Nishiuchi, H. Okuyama, K. Sugita,
S. Takeda, K. Sekizawa and K. Nakagawa

Research subjects in this labolatory are as follows.

(1) Concerning the low temperature electrorefining of aluminum in the molten salt mixtures of aluminum chloride and sodium chloride at 200°C, the anodic dissolution of crude alloys containing silicon and iron are being investigated by potentiostatic electrolysis, chemical analysis and EPMA.

(2) Laboratory scale tests for electrowinning of liquid aluminum are also being carried out by using alkali chlorides molten salts containing aluminum chloride in the temperature range from 700° to 800°C.

(3) Electrodeposition of iron in acidic ferrous sulfate solution containing trace amounts of metal or metalloid ions which functions as an inhibitor in the hydrogen evolution reaction is being studied by means of coulometry and chemical analysis.

(4) Concerning electrolytic treatments of waste water from metal plating processes, a bi-polar close-packed cell is developed and various fundametal studies are also in progress.

(5) Effects of heat transfer on the pitting corrosion of stainless steels and of aluminum are being clarified in ferric chloride and sodium chloride solutions.

(6) In order to elucidate the effects of surface preparation and pretreatments on the anodic polarization behavior of stainless steel, electrochemical studies are in progress by means of potentiodynamic polarization at various potential sweep rates.

Professor Ishikawa attended the Japan-USA Joint Seminar on the passivity of iron and iron-base alloys held in Honolulu, Hawaii, USA in March and the 6th International Congress on Metallic Corrosion held in Sydney, Australia in December.

Dr. Notoya have been studying the mechanisms of corrosion and inhibition of copper and copper alloys with G. W. Poling at the University of British Columbia under the INCRA project since November in 1973. The reseach work at the UBC had terminated November 1975. During staying in Canada, Dr. Notoya attended the Symposium of Electrochemical Society in Toronto in May and the Annual Meeting of CIM in Edmonton in August, 1975.

Oral Presentation

Corrosion of SB steel under boiling heat transfer conditions ; S. Konda, Z. Sagawa T. Ishikawa : 10th Annual Meeting of the Corrosion Reseach Association in Hokkaido, Feb., 1975.

Tempearture Scanning Measurement of the Passivity of Stainless Steel ; T. Ishikawa : 1st Japan-USA Seminar on the Passivity of Iron and Iron-base Alloys (Honolulu), March 1975.

Morphology of Electrodeposited Solid Aluminum from Molten Salts containing Aluminum Chloride. —Application of Rotating Cylindrical Electrode Method— ; T. Ishikawa, T. Matsuda and R. Midorikawa : 42nd Annual Meeting of the Electrochemical Society of Japan, April 1975.

Effect of Presence of Zinc Ion on the Rate of Electrodeposition Iron ; T. Ishikawa and Y. Karikome : *ibid.*, April 1975.

Fundamental Studies on ALCOA New Smelting Process (Part 1) Cation Effect of Alkali Chloride on the Breakdown of Graphite Cathode ; T. Ishikawa, T. Abe and S. Konda : 9th Symposium on Molten Salt Chemistry, Nov., 1975.

Improvement and Its Evaluation on the Form of Solid Aluminum electrodeposited from the Molten Salts containing Aluminum Chloride ; T. Ishikawa, T. Matsuda and R. Midorikawa : *ibid.*, Nov., 1975.

Corrosion and Inhibition of Copper and Its Alloys: T. Notoya; Official Seminar of the University of British Columbia, Department of Metallurgy, Nov., 1975.

Electrolysis of Aqueous solution by bi-polar close-packed cell —Effect of Thickness of Graphite-beads Layers—; T. Sasaki, S. Nishiuchi and T. Ishikawa: 2nd Hokkaido Section Meeting of Electrochemical Society of Japan, Dec., 1975.

Electro efining of Solid Aluminum in the Molten Salts containing Aluminum Chloride —Dissolution Behaviors of Crude Aluminum Anode—; O. Yamamoto and T. Ishikawa: *ibid.*, Dec., 1975.

Effect of Heat Transfer on Pitting Corrosion of Stainless Steels; T. Ishikawa: 6th International Congress on Metallic Corrosion (Sydney), Dec., 1975.

PHYSICAL METALLURGY LABORATORY

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

Graduate Students

M. Uetsuka, S. Kikuchi, N. Yokoya, T. Sawada,
S. Ohnuki and T. Niiyama

Undergraduate Students

T. Hara, K. Kasama, T. Edamura, S. Okazaki
and T. Hasegawa

Influence of irradiation of accelerated electron and neutron on the mechanical behavior and structure of ferrous alloys and bcc metals is intensively studied. Electron irradiation is carried out in 650 kV high voltage electron microscope, so that the structural change due to irradiation is easily detected in situ. It was found that interstitial carbon atoms interact with point defects produced by irradiation, resulting in retardation of precipitation of carbide. JMTR (Japan Material Testing Reactor) at Ōarai, Ibaraki, is used for neutron irradiation. Defect clusters and voids produced in Fe–C alloys during neutron irradiation were found to bring forth hardening. Detailed examination of structure on the irradiated material is being carried out.

Stress corrosion cracking of stainless steel and titanium is investigated by using electrochemical methods including a high speed straining electrode method and a scanning electron microscopy. Statistical nature of pitting corrosion is being studied. Stochastic approach is found to be necessary for understanding many things remanining unsolved in pitting corrosion phenomena.

Professor Takeyama presented a paper on radiation damage of ferrous alloys at the International Conference on Radiation Effects and Tritium Technology for Fusion Reactors and the the International Conference on Fundamental Aspects of Radiation Damage in Metals, both of which are held at Gatlinburg, Tennessee, USA. After the conferences he visited Department of Materials Science and Engineering at North Western University in Evanston, Illinois, and also Department of Metallurgical Enginnering at Michigan Technological University in Houghton, Michigan, where he gave a seminar on radiation damage.

Dr. Shibata joined the US-Japan Seminar on Passivity and Its Breakdown on Iron and Iron Base Alloys at Hawaii, USA, and presented a paper on the analysis of straining electrode behavior of Fe–Cr–Ni alloys. He also attended the 6th International Congress on Metallic Corrosion at Sydney, Australia, presenting a paper entitled "Anodic Activity of Pure Iron Depending on Strain and Straining Rate".

Oral Presentations

Straining Electrode of Mo-containing Stainless steel; M. Kobayashi, T. Shibata and T. Takeyama: 1st Meeting of the Hokkaido Section of the Japan Electrochem. Soc., Dec., 1974.

The Interaction between Defects Produced during Electron Irradiation and Interstitial Solute Atoms; H. Takashi and T. Takeyama: The Hokkaido Section Meeting of the Japan Applied Physics, Jan., 1975.

Electron Irradiation Damage in Steel; T. Takeyama, H. Takahashi, Y. Sato and S. Mochizuki: The Hokkaido Section Meeting of Japan Society for Electronmicroscopy, Feb., 1975.

Statistical Nature of Pitting Corrosin Phenomena; T. Shibata and T. Takeyama; The 10th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1975.

Plastic Deformation and Reactivity of Passive Metals; T. Shibata and T. Takeyama: The US–JAPN Joint Seminar on Passivity and Its Breakdown on Iron and Iron Base Alloys, Mar., 1975.

Electrochemistry of Oxgen Reduction; T. Shibata: The 13th Seminar on Corrosion and It's Protection sponsored by Japan

Electrochem. Soc., Apr., 1975.

Discontinuous Deformation of Iron in the Workhardening Region ; H. Takahashi, T. Takahashi and T. Takeyama : The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute of Japan, May,, 1975.

Comparision of Stress Corrosion Craking and Straining Electrode Behavior of Mo-containing Stainless Steel ; T. Shibata, M. Kobayashi and T. Takeyama : Annual Conference of the Japan Society of Corrosion Engineering, May., 1975.

Interaction between Interstitial Solute Atoms and Defects Produced by Electron Irradiation ; T. Takeyama and H. Takahashi : The Seminar on Refractory Metals and Materials sponsored by the Japan Insittute of Metals., Jun., 1975.

Effect of Interstitial Impurity on High Temperature Deformation in BCC Metals ; H. Takahashi and T. Takeyama : *ibid.*, Jun., 1975.

Irradiation Hardening and Annealing in Irons at a High Neutron Fluence ; T. Takeyama, H. Takahashi and N. Yokoya : Intl. Conference on Radiation Effects and Tritium Technology for Fusion Reactors, Oct., 1975.

Effect of Electron Irradiation on Precipitation of Carbon & Nitrogen in Alpha Iron ; T. Takeyama and H. Takahashi : Intl. Conference on Fundamental Aspects of Radiation Damage in Metals, Oct., 1975.

Temperature Dependence of the Lüders Propagation Velocity of α-Iron ; N. Yokoya, T. Miyama, H. Takahashi and T. Takeyama : The Fall Meeting of the Japan Institute of Metals, Oct., 1975.

Effect of Serration on Work-hardening Behavior in α-Iron ; H. Takahashi, T. Takahashi and T. Takeyama : *ibid.*, Oct., 1975.

Statistical Variation of Pitting Potential ; T. Shibata annd T. Takeyama : The Fall Meeting of the Japan Institute of Metals, Oct., 1975.

Study of Statistical Nature of Pitting Corrosion Phenomena by means of Multichannel Pitting Corrosion Tester ; T. Shibata,

T. Takeyama and T. Wakabayashi: 22th Symphosium of Corrosion and Protection, Oct., 1975.

Anodic Activity of Pure Iron Depending on Strain and Straining Rate; T. Shibata and T. Takeyama: 6th Intl. Cong. on Metallic Corrosion, Dec., 1975.

Construction of Mutichannel Pitting Corrosion Tester and Its Application; T. Shibata and T. Takeyama: 22nd Meeting of the Hokkaido Section of the Japan Electrochem. Soc., Dec., 1975.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Dr. H. Takahashi, Mr. H. Tamura,
Mr. H. Konno, Mr. Y. Otake, Mr. N. Kameda
and Miss T. Ikeno

Students

K. Takahashi, Y. Sato, M. Koda, N. Nishitani,
M. Oshima, D. Nishihira and T. Sato

Research being conducted at present is connected with the anodic oxidation of metals in aqueous solutions and the cathodic deposition of metals from chelate solutions. Air-oxidation of ferrous ions in aqueous solution has also been investigated to explain the effect of anion and the reaction product. An ESCA-AUGER apparatus was recently installed at one of our laboratory rooms by the aid of the Ministry of Education of Japan. Undoubtedly, this apparatus is useful for all of the corrosion scientists in Hokkaido Univ. Nagayama attended the US-Japan joint seminar on "Passivity of Iron and Iron-base Alloys" held in Honolulu and also attended the 6th International Congress on Metallic Corrosion held in Sidney. Dr. A. Rauscher, an assistant professor at the Szeged University, Hungary, is staying with us for one year to work on the passivity of iron in neutral solutions.

Topics of work we are dealing with are as follows:

(1) Formation of "barrier-type" anodic oxide films on aluminum. Oxide films are formed both by galvanostatic and potentiostatic methods in a neutral boric acid-borate solution. Dissolution characteristics, structural feature and composition profile of the film are being examined as functions of temperature, applied current or valtage and time of anodization.

(2) Deposition of coper from copper-pyrophoshate solutions. The cathodic polarization curves have been measured as functions of temperature, solution composition and pH. The adsorption behav-

ior of pyrophosphate ions on copper electrode and the effect of NH_3 are being examined by using ESCA and EPMA.

(3) Air-oxidation of ferrous ion in neutral solutions. Effect of anions such as ClO_4^-, Cl^-, Br^-, CO_3^{2-}, SO_4^{2-}, F^-, and $H_2PO_4^-$ on the reaction rate has been studied in detail. Effectsof amorphous iron (III)-hydroxide, the reaction product, and some crystalline hydrous oxides of Fe(III) are also being examined with the hope of understanding the rusting process of iron.

(4) Passivity of iron in a neutral solution. Passive iron specimens in a neutral borate solution are partially reduced by cathodic treatment and they were reanodized in the same solution. The amount of dissolved ferrous ions during the cathodic treatment is being measured.

Oral Presentations

Spectrophotometric Determination of Iron with Ferron; H. Tamura, Y. Sato, M. Nagayama and K. Goto: The 1975 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Jan., 1975.

Dissolution Behavior and Porosity of Anodic Oxide Films on Aluminum; M. Koda, H. Takahashi and M. Nagayama: *ibid.*, Jan., 1975.

Transport of Ions across the Anodic Oxide Films on Valve Metals during Their Formation; H. Takahashi and M. Nagayama:

The 10th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1975.

Mechanism of Copper Deposition from Pyrophosphate Baths with Ammonia; H. Konno and M. Nagayama: *ibid.*, Feb., 1975.

Distribution of Anion and Proton across the Barrier Layer of a Porous Anodic Oxide Film on Aluminum; M. Nagayama and H. Takahashi: US-Japan Seminar on Passivity and Its Breakdown on Iron and Iron-base Alloys, Honolulu, Hawaii, Mar., 1975.

Air-oxidation Rate of Ferrous Ions on Hydrous Ferric Oxide; H. Tamura and M. Nagayama: The 42nd Annual Meeting of

Japan Electrochem. Soc., Apr., 1975.

Transportation of Al^{3+} and O^{2-} Ions across the Barreier Layer of a porous Anodic Oxide Film on Aluminum ; H. Takahashi, M. Koda and M. Nagayama : *ibid.*, Apr., 1975.

Deposition of Copper from Pyrophosphate Baths with Ammonia ; H. Konno and M. Nagayama : *ibid.*, Apr., 1975.

Reaction between Iron Ion and Ferron in the Presence of a Surface Active Agent ; Y. Sato, H. Tamura, M. Nagayama and K. Gots : The 1975 Summer Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Chem. Soc. for Anal. Chem., July 1975.

Leakage Current Flowing during Formation of a Barrier-type Anodic Oxide Film on Aluminum ; H. Takahashi, T. Ujiye, D. Nishihira and M. Nagayama : *ibid.*, July 1975.

Adsorption of Pyrophsphate on Copper during Its Deposition from Pyrophosphate Solutions ; H. Konno and M. Nagayama : *ibid.*, July 1975.

Coulometric Measurement of the Porosity of Porous Anodic Oxide Films ; H. Takahashi and M. Nagayama : The 24th Annual Meeting of the Japan Soc. for Anal. Chem., Oct., 1975.

Effect of Temperature on the Formation of Barrier-type Oxide Films on Aluminum ; H. Takahashi, D. Nishihira and M. Nagayama : The 2nd Hokkaido Section Meeting of the Japan Electrochem. Soc., Dec., 1975.

Effect of $Fe(OH)_3$ on the Air-oxidation of Ferrous Ions in Neutral Solutions ; H. Tamura and M. Nagayama : *ibid.*, Dec., 1975.

Distribution of Phosphate Ions in Anodic Oxide Films Formed on Aluminium in Phospharic Acid Solution ; M. Nagayama and H. Takahashi : The 6th International Congress on Metallic Corrosion, Sidney, Australia, Dec., 1975.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

T. Nagasawa, K. Matsushita, Y. Sugawara, Y. Matsumoto,
A. Ando, T. Fujimura, Y. Ishii, S. Kudo, M. Saito,
T. Saruwatari and N. Yokoyama

Research activities of this laboratory are concerned with the properties of engineering materials for machinery such as the rupture strength of cast iron, the growth of cast iron at high temperature, and the impact strength of steels heat-treated. Main researches in progress are listed as follows:

(1) The rupture strenght of T-beam was calculated theoretically and the effect of ribs was illustrated as a function of the rib-web dimension ratio. The result was then examined experimentally for FC35 class cast iron.

(2) A formula proposed previously for the practical bending strength of a rectangular beam of cast iron is modified theoretically to apply it to a round bar. The formula leads to the bending strength of a round bar, which is one and one-tenths as large as that of a rectangular beam of the same tensile strength.

(3) The stress concentration factor in cast iron plates with round notches was analyzed by FEM calculation. Owing to the non-elastic property of cast iron, the stress concentration is relieved as much as 20～30% in comparison with elastic metals.

(4) The deflection in the transverse test of cast iron round bar was related theoretically to the stress or load applied. According to the experimental examination, the actual rupture deflection was increased to the level 1.1～1.2 times as large as the

theoretical value estimated by assuming that the bending rupture strain is equal to the ultimate tensile strain.

(5) The growth and structural change of cast iron in CO atmosphere were observed by using SEM and XMA and the dilatation curve was measured. Carburization in CO atmosphere accelerated the growth of cast iron during cyclic heating.

(6) SEM fractography was used to observe the growth of flake qraphite cast iron. As it grew, the matrix of iron reduced and became undistinguishable. The surface of graphite flake was grooved to have hexagonal lines, and as it grew further, the surface roughness increased owing to the interaction with oxidizing atmosphere.

(7) The fracture surface of grown S.G. iron was analyzed by using XMA equipped in SEM. In the surface zone of the grown iron, where pearlitic rings were observed, oxygen and silicon were concentrated around graphite nodules. In the core of specimen both oxygen and silicon were distributed uniformly, while the distribution of carbon was non-uniform.

(8) Thermal conductivity of cast iron was changed with cyclic heating. Tests were carried out on flake and nodular graphite iron specimens. The coductivity of flake graphite iron as cast was reduced remarkably with cyclic heating and the value reached the same level as that of grown S.G. iron after 8% linear growth.

(9) Miscellaneous researches are being carried out on the following subjects :

a) Effects of tempering condition on the hardness and impact strength of steels.
b) Rupture strength of cast iron disc.
c) Self carburization in sintered iron containing graphite.
d) Low temperature impact strength of S.G. iron.
e) Precise tests of tensile and compressive strength in cast iron at low temperatures.
f) Growth of cast iron in hydrogen atmosphere.
g) Effects of oxygen concentration in heating atmosphere on the growth of cast iron.

h) Bending creep of heat-treated steel.

(10) Failure analysis was carried out of an accident of crane resulted from fracture of a pin in roller chain.

Oral presentations

On the Stress Concentration Factors in Notched Cast Iron Plates; T. Noguchi and K. Nagaoka: The 87th Grand Lecture Meeting of The Japan Foundrymen's Society, May 1975.

Growth of Cast Iron in Dilute Oxygen Atmosphere; M. Sōma and K. Nagaoka: The 87th Grand Lecture Meeting of The Japan Foundrymen's Society, May 1975.

Safety of Transporting Machine and Members; K. Nagaoka: Lecture Meeting on Labor Safety, June 1975.

Experimental-Theoretical Analysis on the Transverse-test on Cast Iron Round Bars; T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1975.

SEM Observation on the Growth of Flake Graphite Cast Iron; M. Sōma and K. Nagaoka: The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1975.

Fractography for Failure Analysis; K. Nagaoka: Lecture Meeting for Students, Kitami Eng. College, June 1975.

Machine Accidents in Service and Safety Engieering; K. Nagaoka: Lecture Meeting on Machine Safety and Controll by J.S.M.E., Sept., 1975.

SEM-XMA Analysis on the grown S.G. iron; M. Sōma and K. Nagaoka: The 88th Grand Lecture Meeting of The Japan Foundrymen's Society, Oct., 1975.

Theoretical Consideration on the Transverse Test of Cast Iron; T. Noguchi and K. Nagaoka: The 88th Grand Lecture Meeting of The Japan Foundrymen's Society, Oct., 1975.

On the Thermal Coductivity Change by Growth in Cast Iron; Y. Matsumoto, T. Noguchi and K. Nagaoka: The 88th Grand Lecture Meeting of The Japan foundrymen's Society, Oct., 1975.

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

H. Narita, H. Hayashi, S. Kato, T. Shindo, E. Okabayashi,
T. Kurachi, K. Kurokawa, S. Miyamae, H. Takai
and Y. Kawaguchi

This laboratory is investigating the physico-chemical problems of nuclear reactor fuels and materials. We are also interested in the application of the nuclear chemical methods to the corrosion research. At present, the research is being carried out on the following:

(1) The kinetic studies of hydride formation on the surface of titanium, zirconium and other metals were made by using the vacuum fusion method, the etching method and the irradiation with the 10–150 KeV deuteron. The concentration distributions of hydrogen in the hydride formed on the surface of these metals were also obtained.

(2) The Mössbauer spectra of various kinds of synthesized iron oxides, hydroxides and oxy-hydroxides were measured, and the effect of the synthesizing conditions on the structure of these iron compounds is being investigated.

(3) Thermogravimetric study of the oxidation of UO_2 into U_3O_8 was made under various heating conditions. Also, the effects of the degree of oxidation of UO_2 on the dissolution rate in the nitric acid solutions of various concentrations is being investigated.

(4) Activation analysis of several metallic materials was performed with a 45 MeV electron linear accelerator. Fairly high sensitivity and accuracy were obtained in the quantitative analysis

of some elements in practical Materials such as hafnium in industrial and nuclear reactor grades zirconiums, and molybudenum and other elements in austenitic stainless steels.

Oral presentations

Oxidative Dissolution of Uranium Dioxide by Potentiostatically Controlled Ferricyanide Ions ; H. Ohashi, T. Isogawa, T. Morozumi : The 1975 Winter Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Anal. Chem. Soc., Jan., 1975.

Kinetics of Titanium Hydride Formation by the Cathodic Polarization in Aqueous Solutions ; T. Shindo, T. Mizuno, T. Morozumi : The 10th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1975.

A Study of Iron Oxides by the Mössbauer Spectroscopy ; T. Morozumi, H. Ohashi : The Seminar of the Hokkaido Section of the Japan Institute of Metals, July, 1975.

Nuclear Reactor as a Corrosion Environment ; T. Morozumi : The 22nd Annual Symposium on Corrosion and Protection, Oct., 1975.

Dissolution of Uranium Oxides in Aqueous Nitric Acid Solution ; H. Ohashi, S. Kato, T. Morozumi : The Fall Joint Meeting of Japan Atomic Energy Society, Nov., 1975.

Oxidation Rate of Uranium Dioxide ; H. Hayashi, H. Ohashi, T. Morozumi : The 1975 Meeting of the Hokkaido Section of the Japan Electrochem. Soc., Dec., 1975.

Influence of the Additives in the Aqueous Solution on the Hydrogen Uptake in Titanium by Cathodic Polarization ; T. Shindo, T. Mizuno, T. Morozumi : *ibid.*

VACUUM SCIENCE LABORATORY

Prof. Dr. T. Yamashina, Assist. Prof. Mr. K. Watanabe, Dr. M. Nagasaka (Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, West Germany), Dr. S. Tanaka (Present address: Department of Chemistry, University of Vermont, U.S.A.), Dr. Y. Fukuda (Pressent address: Department of Physics, University of Maryland, U.S.A.), Dr. M. Mohri Mr. M. Hashiba and Mrs. Y. Hirohata

Students

E. Uyeda, M. Yabumoto, H. Kakibayashi, Y. Saito,
M. Sasaki, K. Nakamura, M. Nishino

In this laboratory, research work on the reactivity of solid surfaces and vacuum engineering is in progress with the following subjects:

(1) Surface composition and catalytic actitvity of clean surfaces of alloys: The structure and properties of active sites on the Cu–Ni alloys are investigated by using ultrahigh vacuum techniques for catalytic activity measurements, Auger electron spectroscopy, and work function measurements.

(2) Flash desorption of adsorbed gases from clean surfaces: To clarify the mechanism of catalytic reactions, flash decomposition of formic acid adsorbed on Ir and W surfaces are being measured by using an ultrahigh vacuum system with a mass spectrometer.

(3) Reaction kinetics of titanium and zirconium with hydrogen, oxygen and nitrogen at very low pressures: Kinetic measurements of metal—gas reactions in the pressure range from 10^{-5} to 10^{-6} Torr and in the temperature range from 600° to 800°C are being made by means of an ultrahigh vacuum microbalance with high sensitivity.

(4) Mechanisms of the formation of oxide- and nitride-films:

Oxide- and nitride-films of molybdenum, titanium, iron and aluminum containing various amount of oxygen and nitrogen have been prepared by a reactive sputtering method. The structure and chemical composition of the films in the partial pressure of oxygen and nitrogen are being investigated to understand the formation mechanism.

(5) Chemical reactivity of nitrogen in the reactively sputtered films of iron nitride: Chemical reactivity of the nitrogen is being measured by using an isotope reaction on sputtered films of iron nitride.

Oral Presentations

Co-isomerizaton of cis-2-butene over La_2O_3 Catalyst; Y. Fukuda, T. Yamashina, H. Hattori and K. Tanabe: The 32nd Annual Meeting of Japan Chemical Society, Tokya, Apr., 1975.

Measurement of Surface Composition of Cu–Ni Alloys by Auger Spectroscopy; K. Watanabe, M. Hashiba, Y. Fukuda and T. Yamashina: *ibid.*

Deposition Process of Thin Films in the Reactive Sputtering (I) —Effect of Sputtering Gas on the Deposition Rate—; T. Abe, F. Tanuma and T. Yamashina: The 22nd Annual Meeting of Japan Society of Applied Physics, Chiba, Apr., 1975.

Deposition Process of Thin Films in the Reactive Sputtering (II) —AlN Films—; Y. Hirohata, T. Abe and T. Yamashina: *ibid.*

Adsorption and Equilibration Reaction of Hydrogen at Very Low Pressures on Evaporated Nickel Films; K. Watanabe and T. Yamashina: The 3rd Japan-Soviet Seminar on Catalysis, Alma-Ata, USSR, June, 1975.

Kinetic Study of High Temperature Oxidation of Titanium and Zirconium at Very Low Pressures; T. Yamashina and M. Nagasaka: The Fall Meeting of Japan Institute of Metals, Sapporo, Oct., 1975.

Effect of Vacuum Annealing on Surface Composition of Cu–Ni Clean Surfaces by Auger Spectroscopy; K. Watanabe, Y. Fukuda, M. Hashiba and T. Yamashina: *ibid.*

In-Depth-Profile of Clean Surface of Cu–Ni Alloys by Auger Spectroscopy; K. Watanabe, Y. Fukuda, M. Hashiba and T. Yamashina: The 36th Fall Meeting of Applied Physics, Fukuoka, Nov., 1975.

Adsorption of Cabon Monoxide over Cu–Ni Clean Surfaces by Auger Spectroscopy; M. Hashiba, Y. Fukuda, K. Watanabe and T. Yamashina: *ibid.*

Observation of Crystal Surfaces by means of SIMS–AES Combined System (Invited Lecture); T. Yamashina: *ibid.*

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

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

Students

K. Nakajima, M. Kurita, M. Kobayashi, K. Chiba,
Y. Okuda and T. Sakurai

This laboratory is concerned with basic and applied researches on pyro- and hydro-metallurgical extractions of nonferrous metals.

Researches in progress are concentrated on the following projects:

(1) Researches on hydrogen production from sulphide compounds

a) Reaction between metal sulphides and water vapour at high temperatures. Thermodynamic and kinetic investigations are being made for the production of hydrogen from sulphide ores.

b) Researches on the production of hydrogen from hydrogen sulphide. Conversion of hydrogen sulphide to hydrogen by molten metals and regeneration of metals from metal sulphides by mutual reaction are being carried out. Cyclic treatments of hydrogen sulphide by combination of following two reactions are also in progress:

$$Fe_3O_4 + 6HCl + H_2S \rightleftharpoons 3FeCl_2 + 4H_2O + S^0$$

$$3FeCl_2 + 4H_2O(g) \rightleftharpoons Fe_3O_4 + 6HCl + H_2$$

(2) Reduction kinetics of metal sulphides by hydrogen. This study is aimed at finding the mechanism of direct reduction of sulphide ores. Observation of the nucleation and growth of reduced metals by scanning electron-microscope, morphologic char-

acteristics of the metals reduced from sulphides, oxides, chlorides, and sulphates, and vapour phase reduction of metal sulphides being made.

(3) Electrochemical measurements in some pressure hydrometallurgy. The reaction kinetics of the oxygen pressure leaching of sulphide minerals and the hydrogen reduction of metal salts in aqueous solutions are being studied by means of polarization measurements of sulphides and metal electrodes in an autoclave under the conditions of temperature up to 200°C and pressure of 50 kg/cm^2.

Oral Presentations

Kinetic study on the reduction of germanium sulphide by hydrogen; H. Kiuchi, K. Harashima, and T. Tanaka: Annual Meeting of the Mining and Metallurgical Institute of Japan, Tokyo, March, 1975.

A study for effective utilization of hydrogen sulphide; H. Kiuchi, F. Saishu and T. Tanaka: *ibid.*, Tokyo, March, 1975.

Fundamental studies on the reaction between metal sulphides and water vapour at high temperatures; R. Shibayama and T. Tanaka: *ibid.*, Tokyo,March, 1975.

Researches on the reaction between ferrous salts and water vapour at high temperatures (II); R. Shibayama and T. Tanaka: The Hokkaido Section Meeting of the Mining and Metallurgical Institute of Japan, Sapporo, June, 1975.

A study for the thermal decomposition of hydrogen sulphide with metal; H. Kiuchi and T. Tanaka: The Hokkaido Section Meeting of the Mining and Metallurgical Instittute of Japan, Sapporo, Nov., 1975.

Researches on the reaction between ferrous salts and water vapour at high temperatures (III) On the dissolution of Fe_3O_4 with hydrochloric acid; R. Shibayama, K. Nakajima and T. Tanaka: *ibid.* Nov., 1975.

Hydrogen recovery from H_2S with molten metals; H. Kiuchi and T. Tanaka: The 2nd Symposium on Hydrogen Energy System, Hydrogen Energy System Society, Tokyo, Nov., 1975.

Fundamental studies on the oxidation of S^{2-} and S^{4+} compounds by water vapour ; R. Shibayama and T. Tanaka : *ibid.*, Nov., 1975.

Hydrogen and future of nonferrous extractive metallurgy ; T. Tanaka, R. Shibayama and H. Kiuchi : Annual Meeting of the Mining and Metallurgical Institute of Japan, Tokyo, Nov., 1975.

The Effect of Electron Irradiation on the Precipitation of Fe–N Alloy

T. Takeyama and H. Takahashi

J. Phys. Soc. Japan, 38, 1783 (1975)

The interaction between the solute atom and the point defect in Fe–N alloy produced by the irradiation of high energy electrons in a high voltage electron microscope (HVEM) was studied in a variety of heat treatment.

The solution quenched Fe–0.03 wt % N alloy was irradiated at the accelerating voltage of 650 kV HVEM in a fluence of 1.8×10^{21} e/cm^2 at the room temperature.

The surrounding un-irradiated area shows a large amount of metastable α'' nitride ($Fe_{16}N_2$). On the other hand, in the central part of 10 μm diameter of irradiated area no such precipitation is observed. Because no precipitation is observed in the irradiated area at 130°C aging, it is considered that the most of N atoms have been trapped in point defects. Presumably, the N atoms are bound mainly in the form of V–N pair and I–N cluster. The former may be composed of one N atom trapped in each vacancy and the latter Fe interstitials and N atoms. The up-quenching heat-treatment was applied to find the dissociation phenomenon of V–N pair which is supposed to occur at lower temperature than the dissociation temperature of I–N cluster.

The lowest temperature of the dissociation of the V–N pair was determined at 200°C as a result of the combined heat-treatments of various up-quenching temperatures and then re-aging at 130°C. This dissociation temperature was lower than that of the V–C pair which was determined as 240°C. (English)

The Effect of the Recovery and Recrystallization Processes on the Mechanical Properties of a Mild Steel

H. Takahashi, H. Uetsuka and T. Takeyama

Bulletin of the Faculty of Engineering,
Hokkaido University, NO. 75, 193 (1975)

The effects of recovery and recrystallization on the mechanical properties of a mild steel were investigated after rolling from 10 to 40% reduction in thickness and annealing in a temperature range from 200 to 800°C.

After annealing below 500°C, both the yield and the ultimate tensile stresses became higher, and the elongation decreased with increasing reduction in thickness. Also, with the rise in annealing temperature above 200°C, the strength decreased gradually and the elongation became larger. Dislocation structures observed after annealing in such a temperature range still showed well-developed cell structures, but were not rearranged into stable low-angle polygonization boundaries, i.e., sub-boundaries.

When the annealing temperature exceeded 500°C, the yield stress and the ultimate tensile stress of the materials after 30–40% rolling rapidly decreased, and in contrast the elongation became very large. While, in material after 10% rolling a relatively larger elongation was obtained without a great decrement of strength even after annealing at elevated temperatures.

From an observation of the corresponding dislocation structures, it was clarified that the change of the mechanical properties of heavily defomed materials contributed to the occurrence of recrystallized grains, and on the other hand high strength and large elongation after annealing above 500°C of the weakly deformed materials took place by the stable subgrain formation. (Japanese)

Effect of Ribs on the Bending Strength of Cast Iron T-Beam

T. Noguchi and K. Nagaoka

IMONO, 47, 2 (1975), Feb.

The theoretical rupture strength of cast iron T-beam was calculated by using an electronic computer with a particular attention to the non-elastic behavior of cast iron. The effect of ribs was illustrated as a function of the rib-web dimension ratio, and the calculated values were checked experimentally.

The effect of ribs on cast iron T-beams may be computed as elastic materials within a certain range of rib-web ratio. The non-elastic property of cast iron, however, must be considered in estimating the effect of ribs beyond the range. In the case of ribs in tension, when the ribs was small compared to the web, the effect of the rib was greater than the value elastically calculated. Thus, the actual rupture strength of T-beam was greater than the value calculated from the section modulus of the beam. In cast iron the range of rib-web ratio that decreased the strength of T-beam was narrower than that for the elastic materials. In the case of web in tension, the beam strength calculated from the section modulus was greater than the actual strength. The narrower and the deeper the ribs was, the greater the discrepancy became.

The effect of ribs changed depending on the grade of cast iron. It was found that when the rib-web ratio was small, the cast iron of low strength behaved as elastic materials.

The calculated value agreed well with the value observed for FC35 class grey iron. The difference between the experimental and the calculated values in deep ribs was explained by a size effect due to the stress gradient in bending. (Japanese)

The Growth of Cast Iron in Carbon Monoxide

M. Sōma and K. Nagaoka

IMONO, **47**, 3 (1975), March

The growth of flaky and nodular graphite iron were examined in carbon monoxide heating atmosphere and the results were analyzed theoretically based on the growth mechanism of irreversible graphite migration proposed by the author.

Growth of flaky graphite iron in carbon monoxde was much greater than that in vacuum. Irreversible dimensional increase of the iron was also observed while heating at constant temperature in austenite region. The grown iron showed structural change due to carburization, that is, the formation of black network in pearlitic matrix. Influence of CO atmosphere on the growth of nodular graphite iron was minor.

Carburization in CO atmosphere accelerated the growth of cast iron during cyclic heating. According to the growth mechanism of nominal volumetric change by the two processes of dissolution and separation of graphite, the carburization in CO increases the dissolution of carbon into austenite and ultimately increases the growth by graphite redistribution. As the black network formed around graphite flake was confirmed by X-ray analysis to be composed of carbon and silicon oxides, the carburization in carbon monoxide may be accompanied with oxidation of silicon in the iron. (Japanese)

Machine Accidents in Service and Safety Engineering

K. Nagaoka

Text of Lecture Meeting on Machine Safety and Control,
Hokkaido Section of J.S.M.E., Sept., 1975

Prevention of machine accident have to keep the preference in machine engineering. The higher the energy level of machine; e.g. higher speed, higher pressure and larger scale, the greater the damage by an accident. Machine accidents in srevice are caused by various factors of disign, manufacturing, operation and safety control. If dangerous factors are foreseen and eliminated, the safety of machine in service would be kept perfectly. Unfortunately, many machine accidents, however, occur in service, and the causes and factors of the accidents are investigated after those happened. In some cases machine accident is caused by human factors, e.g., operation error and miss judgment. Therefore, the investigation of the cause may be complicated.

Failure analysis of machine member consists of two stages of metallurgical and mechanical procedures. Fractography applied to a failed part would show metallurgically the origin of failure and some mechanical conditions in an outline. Mechanical failure analysis is applied to the initiation of failure to determine the quantitative conditions of the failure; i.e. the safety factor analysis and life check are carried out.

As some factors of failure which are not noticed to be dangerous may cause a serious accident, application of failure analysis to the machine with slight troubles is very important to prevent it from an accident. (Japanese)

Some Problems on the Mechanical Behavior of Cast Iron

T. Noguchi and K. Nagaoka

Journal of the J.S.M.E., 78, 684, Oct., 1975

According to the remarkable development in production and metallurgy, the mechanical properties of cast iron have been also studied widely for machine design and reliable usings. However, the mechanical properties of cast iron, such as low notch sensitivity, low tensile strength, high compressive and bending strength, are not yet clarified theoretically. As cast iron is non-elastic metal, the fundamental behavior differs from that of steel and copper, and the stress and strength are not calculated from the usual elastic theory.

Stress analysis based on the nonlinear stress-strain relation of cast iron showed that the beam was ruptured by 10~25% higher bending moment than that estimated from the maximum stress theory. Ratios of measured rupture bending moment to theoretically calculated one changed with the shape and size of beams. The practical bending strength σ_b of rectangular beam and round bar is well related to the tensile strength σ_t. For a rectangular beam the relation is formulated by $\sigma_b=\{(2.0-(\sigma_t/100)\}\times\sigma_t$, (kg/mm^2), but for a round bar σ_b is estimated to be 10% higher.

The notch-strength of a cast iron was about 70% of unnotched strength, and the notch-strength varied with the grade of cast iron and the profile of the notch. According to the FEM calculation, the rupture strength of dull notched cast iron was explained well by the maximum stress theory. On the other hand, in sharply notched specimens the modified average stress criterion was valid. (Japanese)

Sulfurization of Iron and Its Alloys at Elevated Temperatures

K. Nishida

Journal of the Iron and Steel Institute of Japan
61, 411 (1975)

This technical review was written in behalf of ISIJ on the sulfurization of iron and its alloys as the corrosion of these metals and alloys are very often observed in some failures. The study on this item has been much attentioned in the recent industry. Accordingly, the trend of the investigation in the past was first retrospected and the present status of the sulfurization study was newly emphasized in comparison with that of the oxidation research of these metals and alloys.

It contains the following: (1) The history of the sulfurization study of metals and alloys, (2) Significance of the sulfurization study, (3) Sulfurization behavior of pure iron in sulfurvapor, (4) Sulfurization behavior of iron-based alloys, (5) Sulfurization of binary iron alloys, (6) Spinel-type and other complex sulfides in the scale formed, (7) Approach to sulfurization of iron and its alloys, (8) The sulfurization behavior in comparison with the oxidation of iron alloys.

However, the present status of the study on sulfurization is still confined to some idealized conditions and there are a number of complex problems to be expected. Therefore, it was finally emphasized that we must further take account of many other physico-chemical properties as well as mechanical behavior of sulfides at elevated temperatures. (Japanese)

Kinetics and Cation Distributions in the Ferrous-Nickel Sulfide Scales on Iron-Nickel Alloys

T. Narita and K. Nishida

Denki-Kagaku **43**, 443 (1975)

Sulfurization of iron alloys containing up to 15.2 wt % Ni was carried out in the temperature range from 560 to 900°C under an atmospheric sulfur pressure. Kinetics of sulfurization, surface morphology and preferred orientation of the grown sulfide scale and also their temperature dependences obtained for the Fe–Ni alloys were shown to coincide well with those of pure iron.

Nickel and iron in the scale concentrated toward the scale-gas and alloy-scale interfaces, respectively, whereas no such concentration change was observed in the alloy substrate.

By making use of Wagner theory the concentration profiles in the sulfide scale were analyzed reasonably and a good agreement between the calculated and observed concentration profiles was obtained when the ratio of self-diffusivities of Ni and Fe($P=D^*_{\mathrm{Fe}}/D^*_{\mathrm{Ni}}$) was supposed to be about 0.6, irrespective of temperature and alloy compositions. Reliability of this P-value was discussed according to the diffusion theory and self-diffusivities of Ni and Fe in their pure sulfides. Accordingly, it was concluded that the theory could be used for the analysis of the concentration profiles in the sulfide scale. (English)

Theoretical Analysis of Cation Distributions in the (Co, Ni) O Scales Formed on Co-Low Ni Alloys

T. Narita and K. Nishida

Journal of the Japan Institute of Metals,
39, 1152 (1975)

Concentration profiles of nickel in the (Co, Ni) O scales grown on the Co-low Ni alloys (0.45, 2.46 and 7.23 wt % Ni) over the temperature range from 1000 to 1300°C were determined by means of EPMA and then analyzed according to the analytical equation after Wagner and the differential equations after Dalvi and Coates.

By making use of both computation methods, the concentration profiles similar to the observed ones were obtained, but an agreement between them was found to be insufficient in the inner part of the scale. The values of $P(D_{Ni}/D_{Co})$ and $n(P_{O_2}^{1/n})$ were determined as a result of the present analytical method and found to be within the range reported in the literature. These values of P and n depended on all parameters, in particular, strongly on ξ' (NiO content at the alloy-scale interface) and $k'(=k/D^0_{Co})$, respectively. In contrast with the presentation by Dalvi and Coates, both P- and n-values changed with NiO content in the oxide.

The mass balance equations at both scale interfaces were used to judge the validity of the numerically obtained solutions. The resulting solutions were unsatisfied with the mass balance equation at the scale-gas interface. Therefore, it was concluded that the perfect solutions could not be obtained by using the equations by Dalvi and Coates. This result may be ascribed to the changes of the P- and n-values with NiO content in the oxide.

On the other hand, the equation by Wagner is suitable for an approximate estimation of cation distribution and cation diffusivities in oxide scales because of its simplified form. (Japanese)

Oxidation Kinetics and Scale Structures of Co–Ni Alloys in the Temperature Range from 1000° to 1200°C

K. Nishida, T. Narita, N. Ohya and T. Yamauchi

Trans. JIM, **16**, 755 (1975)

Co–Ni alloys over the whole composition range were oxidized over the temperature range from 1000 to 1200°C under 1 atm of pure oxygen. Kinetics, internal oxidation, surface morphologies, and concentration profiles in the cross sections were investigated by means of thermogravimetry, X-ray diffraction, optical microscopy, and electron probe microanalysis.

Results obtained ara as follows:

(1) The oxidation rate constants, which were determined by batch type measurements of weight gain and scale thickness, decreased exponentially with nickel content in the oxide scale.

(2) In all specimens Ni and Co in the grown oxide scale were concentrated near the alloy-scale and scale-gas interfaces, respectively.

(3) Concentration profiles of Co and Ni in the scale and alloy substrate can be represented by one master curve when the concentration was plotted against $x/\sqrt{t}$.

(4) Internal oxidation and depletion of cobalt in the alloy substrate were found in the nickel-rich alloys, resulting in the enrichment of cobalt in the oxide scale. The growth rate of the depletion zone of cobalt depended not on the alloy composition but on the temperature. The apparent activation energy of the growth was about 72 kcal/mol which was close to those of oxygen- and inter-diffusivities in the Ni–Co alloys.

From the present results and other authors' studies, the alloy composition-temperature diagram of the oxidation behavior was schematically shown. (English)

Corrosion Behavior of Iron and Low Carbon Steels in Molten Alkali Nitrates Containing Alkali Halide

T. Notoya, T. Ishikawa and R. Midorikawa

Proc. 5th Intern. Congr. Metallic Corrosion,
pp. 1039–1043, NACE (1974)

The oxidation behavior of iron and low carbon steels in molten alkali nitrates in the presence and absence of potassium halide has been studied gravimetrically at 350°–470°C. Iron oxide scales grow parabolically in molten nitrate, while they grow linearly with time in the presence of halide. The corrosion rate of iron increases with increasing halide concentration and depends on the type of anions present in the melt, of which aggressiveness increases in the order, I^-, Br^-, Cl^-. Chemical analysis and EPMA measurement indicate the presence of halide in the oxide layer. It is suggested that the corrosion behaviors of metals in the systems are similar to those of high-temperature corrosion in an oxidizing gas with or without halogen gas. (English)

Mechanism of Formation and Dissolution of Anodic Oxide Films of Aluminum in Acid Solution

M. Nagayama, K. Tamura and H. Takahashi

Proc. of the 5th International Congress on Metallic
Corrosion, NACE (1974), pp. 175

Anodizing of Al was carried out in oxalic acid-oxalate solutions over the pH range from 1.7 to 6.4 at constant anodic potentials and time-variations in the anodizing current, the structure of the film and the amount of dissolved Al ions were observed. The current-time curve was divided into four successive periods of a, b, c, and d in releation to the surface structure of the film. In the initial period of anodizing (period a), the current falls nearly exponentially with time in accordance with the growth of the barrier layer. After a certain period of time the lowering of current ceases (period b) and the current begins to increase with time (period c) and finally reaches a steady value (period d), owing to the pore initiation and the growth of the porous layer. It was found that an appreciable amount of oxide dissolves even in the period a ; the rate of dissolution is affected strongly by the anion species in the solution but scarcely changes with the pH of the solution. A high rate of dissolution observed at periods c and d increased remarkably with increasing anode potential and with decreasing pH. This is explained in terms of the mechanism which assumes the formation of cation defects at the outermost part of the barrier layer and their interaction with protons in the solution. (English)

Anodic Oxidation of Zirconium

T. Morozumi and M. Moriya

Proceedings of the Fifth International Congress on
Metallic Corrosion. 322–325 (Copyright 1974)

The anodic polarization characteristics of zirconium were measured in 1 N ammonium nitrate, saturated ammonium borate, 0.1 N sodium hydroxide and 0.5 N sodium sulfate by the potential sweep and the galvanostatic transient methods. A peculiar property that the electrochemical evolution of oxygen on the zirconium surface virtually stops at relatively high oxygen overpotential was recognized. The anodic oxygen evolution in most of the cases started at more noble potential, 1.0 V vs, S.C.E., and stopped at higher potentials than 2.0 V vs, S.C.E.. A deviation from the linear relation between the reciprocal electrode capcitance and the potential was observed in the potential region from 1.0 to 2.0 V. However, no remarkable change of the electron diffraction pattern of the surface oxide with the electrode potential in this potential region.

An explanation of this abnormal phenomenon was given on the basis of the electronic theory which was conducted by T. E. Hartman for the tunnel electronic conduction in the metal/insulator/metal system. (English)

Anodic Passivation of Cobalt in Neutral Solutions

T. Ohtsuka and N. Sato

Journal of the Japan Institute of Metals,
39, 60 (1975), No. 1.

A bare surface of cobalt was anodically oxidized at constant potential in neutral, deaerated boric acid-sodium borate solutions of pH 7.45 to 11.0, and the anodic oxide film was cathodically reduced at constant current to analyze the composition of the film.

The anodic polarization and dissolution curves exhibit the active dissolution of cobalt, the primary passivation in a potential range from $(+0.15\sim0.058\,\mathrm{pH})$ V to $(+0.86\sim0.058\,\mathrm{pH})$ V against SHE, the secondary passivation in a potential range from $(+0.86\sim0.058\,\mathrm{pH})$ V to $(1.45\sim0.058\,\mathrm{pH})$ V and the oxygen evolution at potentials more positive than $(1.45\sim0.058\,\mathrm{pH})$ V. The primary passive film is identified as CoO or $\mathrm{CoO}\cdot n\mathrm{H_2O}$ and its thickness is estimated by coulometry to be 12∼20 Å almost independent of the potential at which the film is formed. The secondary passive film is determined from the rate of cathodic-reductive dissolution as a spinel-type oxide $\mathrm{Co_3O_4}$ and its thickness increases with rising potential. Above 1.10 V in the oxygen evolution region, the trans-passive dissolution occurs producing a thick oxide film probably consisting of a cobaltic hydroxide CoOOH. (Japanese)

The Passive Oxide Films on Cobalt in Weakly Alkaline Solution

T. Ohtsuka and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
24, 289 (1975), No. 6.

Anodic oxide film formed on cobalt in sodium borate solution at pH=11.0 have been investigated by coulometry and potentiometry. The potential change during galvanostatic oxidation exhibits three plateaus before the potential reaches a steady state value for oxygen evolution reaction. In the first plateau $Co(OH)_2$ is formed on cobalt. Further oxidation at constant current leads to a potential rise which accompanies the formation of CoO layer between the cobalt metal and the $Co(OH)_2$ film. In the second plateau a reaction of $CoO \cdot nH_2O$ to Co_3O_4 occurs with a coulomb equivalent to the reaction. This Co_3O_4 film is oxidized to $Co_2O_3 \cdot mH_2O$ in the third plateau, the potential of which is 0.575 V (she) not depending on the current densities and probably corresponds to the equilibrium potential of $Co_3O_4/CoOOH$. This change of Co_3O_4 to $Co_2O_3 \cdot mH_2O$, however, does not complete during the potential arrest at the third plateau. From the galvanostatic-cathodic reduction of the films formed at constant potential and at constant current, the primary passive film formed in the potential range from −0.455 V to +0.22 V (she) is estimated to be $CoO \cdot nH_2O$, the secondary passive film in the range from +0.22 V to +1.1 V to be mainly Co_3O_4, and the transpassive film at potentials more positive than 1.1 V to be Co_3O_4 and $Co_2O_3 \cdot mH_2O$. In the potential region of the secondary passivity (0.2 V to 0.45 V), both $CoO \cdot nH_2O$ and Co_3O_4 are formed under potentiostatic conditions and the ratio in amount of Co_3O_4 to $CoO \cdot nH_2O$ increases with rising potential. In this potential region, $CoO \cdot nH_2O$ is first formed and then gradually changes to Co_3O_4 at constant potential. (Japanese)

On Dry and Wet Corrosion of Iron

M. I. Ismail and N. Sato

Bulletin of the Faculty of Engineering,
Hokkaido University, **75**, 169 (1975)

Metallographic and polarographic techniques were used to study the rule played by metal substrate metallurgical conditions on corrosion of pure iron. Different heat treatment cycles were employed, viz: 1 hour at 600–900°C, 10^{-3} Torr, rapidly cooled (WQ), or slowly furnace cooled (FC), or rapidly heated specimens in air (30 sec, 1000°C, air cooled); and the effect of heat treatment cycling. It was found that the oxide film formed in air has random orientation while the one formed in vacuum is oriented. The anodic current decay during polarization, the amount of dissolved metal and surface morphology were used to clarify the effect of heat treatment in corrosion of iron. (English)

Oxygen Reduction and Corrosion

T. Shibata

Surface (Hyōmen), **13**, 460 (1975)

This review describes oxygen reduction characteristics on various metals and oxides, intending to clarify the mechanism of corrosion of iron in neutral solutions. Hydrogenperoxide as an intermidiate product plays an important roll to reduce an efficiency of reduction. Various factors to affect production of hydrogenperoxide are discussed with respect of pH, metal, and surface oxide. OH^- production as a final product makes corrosion rate decrease through precipitation reaction on the surface combining with dissolved iron ion. In addition to precipitation reaction on the surface, oxidation of Fe^{++} due to dissolved oxygen is pointed out to be studied for complete understanding of corrosion process of iron in neutral solutions. (Japanese)

Chemical Property of Materials
—Stress Corrosion Cracking—

N. Sato

J. Chem. Eng. Japan (KAGAKU KŌGAKU),
39, 166 (1975)

This article is an introductory review of SCC to chemical engineers. SSC is a mechanochemical reaction that occurs at a limited site where both mechanical stress and chemical activity are enhanced. It is therefore a localized phenomenon, and its stability or instability depends not only stress distribution in materials but also nonhomogeneity of agressive environments. The fracture mechanics approach to SCC and hydrogen embrittlement is also reviewed. It is illustrated schematically that the stress corrosion crack mode of stainless steels changes depending on the electrode potential. (Japanese)

Application of High Speed Elongation Technique to Stress Corrosion Cracking of Fe–Cr–Ni Alloys

T. Shibata and R. W. Staehle

Proc. 5th Intl. Cong. on Melallic Corrosion, pp. 487
NACE, Houston, Texas (1974)

A high speed elongation technique has been developed to measure the transient current during elongation and used to prove a restricted lateral dissolution criteria for stress corrosion cracking, proposed by Staehle and Latanison. This technique can measure the anodic current density of initial dissolution and of film formation on a newly created surface. It was found that high susceptible alloys to stress corrosion cracking in boiling magnesium chloride solution showed the high dissolution current or low film formation current in borate solution. That is, the ratio of $i_{100}/i_{\max}$ correlates to the time to failure of the alloy (T_f) as follows,

$$T_f = k(i_{100}/i_{\max})^n$$

where k and n are constants. The role of minor elements added to alloys was explained by either the metallurgical factor controlling the surface slip step morphology or by the chemical factor affecting repassivation rate of the film based on the change of i_{100} or $i_{\max}$. Critical role of chloride ions was also discussed from their influences on repassivation rate rather than on the dissolution rate at the tip. (English)

The Role of Straining in the Electrochemical and Mechanical Behaviour of Pure Iron

M. I. Ismail and N. Sato

Bulletin of the Faculty of Engineering,
Hokkaido University, **57**, 181 (1975)

The effect of straining and its rate on the corrosion behavior of heat treated (800°C for one hour followed by furnace cooling or water quenching) pure iron was studied by measuring the anodic current density (cd) of potentiostatically polarized specimens in 0.1 N H_2SO_4 at 20°C. Results, thus obtained, show that there are critical points in the relation, cd-strain rate. These points depend on metallurgical conditions of the metal substrate. Furnace cooled (FC) specimens have a maximum cd at a certain strain rate and passive potential (1200 mV), while at active potentials (600 mV) there exists a minimum. Water quenched (WQ) specimens always have a minimum cd at a certain rate.

In the relation of cd to strain at the same strain rate, there is a certain strain at which the average grain size of metal is larger, and at this critical strain cd is lowest (minimum). At these critical strain rates, the yield stress is also lowest (minimum), but the total strain is independent of strain rate. An identification of crystallographic, pitting and active modes of attack has been made. It is emphasized that metallographic conditions play an important role in this type of corrosion of iron. (English)

Effect of Temperature and Heat Transfer on Corrosion of steels in Acidic Soluttions

T. Ishikawa and R. Midorikawa

Proc. 15th Intern. Congr. Metallic Corrosion,
pp. 997–1001, NACE (1974)

The values of apparent activation energy as a measure of temperature effect on the corrosion rate of iron and steels are determined in the nitrogen-saturated acidic solutions by the controlling process in the corrosion reaction. For activation-controlled systems, it was found to be around 15 kcal/mol. and for diffusion-controlled systems around 3.5 kcal/mol., respectively. The corrosion rate under heat transfer condition changed not only with the surface temperature, but also with the magnitude and direction of heat transfer. Some procedures for substracting the heat transfer effect from the surface temperature effect were proposed. According to these procedures, it was found that the corrosion rate in a nitrate solution depends only on the surface temperature and is almost independent of the magnitude and direction of heat flux. In chloride solutions and sulfate solutions the corrosion rate depends not only on the surface temperature, but also on the magnitude and direction of heat flux. In other words, the corrosion reaction was stimulated when the heat flux was in the same direction as metallic ion transfer, but suppressed when the heat flux was in the opposite direction to the metallic ion transfer. (English)

Estimation of Corrosion Velosity of Steel in Neutral Solution by Polarization Resistance Measurement

M. Nagayama, K. Goto and Y. Otake

Proc. of the 5th International Congress on Metallic
Corrosion, NACE (1974) pp. 1061

The use of polarization data in estimation of the corrosion rate of metals is discussed. The anodic polarization measured by applying a constant current for several seconds is found to be closely connected with the corrosion rate, and a special normalization method was developed to obtain the corrosion rate. It is shown that the established method can be applied with success in examining the corrosion behavior of steels in neutral solutions containing inhibitors. (English)

Kinetic Studies on the Leaching of Pyrite with Plate Specimens

——Studies on the Pressure Leaching of Pyrite (2nd Report)——

T. Nagai and H. Kiuchi

Journal of the Mining and Metallurgical Institute
of Japan, **91**, 473～477 (1975) No. 1049

Kinetic studies on the pressure leaching of pyrite in 1N–H_2SO_4 solution were made by using plate specimens cut out from natural single crystals. No significant change of the geometric, macroscopic area of the specimens was observed and the dissolution rate was constant during any run of experiments.

The surface of the specimens which has been subject to leaching experiments at low temperature or low oxygen pressure exhibited bamboo leaf-like etch figures, whereas the pyramidal etch hills reported previously were observed at high temperature and pressure. The transformation of these etch figures occurred at the leaching temperature near 145°C or at the oxygen pressure of about 5 kg/cm^2. Strong stirring of the solution disturbed the formation of pyramidal etch hills and such effective stirring accelerated the reaction rate, while the reaction seemed to be under activation control. Temperature and oxygen pressure-dependencies of the reaction rates showed discontinuities at the same temperature or pressure as those at which the transformation of etch figures was observed.

These observations were discussed and interpreted by the dissolution model of pyrite proposed in our earlier papers. (Japanese)

Electrochemical Studies on the Pressure Leaching

—— Studies on the pressure leaching of pyrite (3rd Report) ——

T. Nagai and H. Kiuchi

Journal of the Mining and Metallurgical Institute
of Japan, **91**, 547~553 (1975) No. 1050

Electrochemical studies on the pressure leaching of pyrite in $1N-H_2SO_4$ solution at high temperature up to 175°C were made by using pyrite electrodes. Reaction products of the anodic polarization in the absence of oxygen were mainly Fe^{2+} and S^0, and the HSO_4^- was also produced in a less degree.

An electrochemical mechanism was proposed by assuming some difference in the density of active sites between the pressure leaching and the anodic polarization experiments. According to the mechanism, the main anodic reaction on the surface of pyrite was the reaction: $FeS_2 \rightarrow Fe^{2+} + 2S^0 + 2e$, and the electrochemical oxidation of sulphide sulphur to sulphate also occurred but in a less degree. Oxygen plays some roles in the mechanism: a) as the cathodic reactant in the main reaction, b) oxidizes the reaction products in the solution and c) provides the chemical process for removal of the S^0 on the reaction sites. The active sites were also provided by physical process which involves the gathering of molten S^0 and the action of stirring stream for cleaning up the reaction surface. (Japanese)

Oxidative Dissolution of Uranium Dioxide by Potentiostatically Controlled Ferricyanide Ions

H. Ohashi, T. Isogawa, T. Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 77, 127 (1975)

The rate of oxidative dissolution of uranium dioxide with ferricyanide ions was measured by the potentiostatically controlled coulometry. The rate and the total amount of the reaction were influenced by many factors including the concentration of ferricyanide, the kind and the concentration of supporting electrolytes, pH and temperature. The main product of the reaction was uranyl ions which formed the complexes competitively with ferrocyanide ions and with the anions of the supporting electrolytes. When the rate of the formation of uranyl ferrocyanide is predominant, an insoluble film produced on the surface of uranium dioxide inhibits further dissolution. Jander's equation was applicable to the initial rate of the reaction, suggesting that the reaction proceeds predominantly by the film formation even in the initial stage. The film formation may be prevented by adoption of other supporting electrolytes which can form a soluble complex of high stability constant with uranyl ions. (Japanese)

Dissolution of Hydrous Chromium Oxide in Acid Solutions

M. Seo, R. Furuichi, G. Okamoto
and N. Sato

Transactions of the Japan Institute
of Metals, **16**, 519 (1975)

The dissolution behavior of precipitated hydrous chromium oxide in perchloric acid solutions containing SO_4^- or Cl^- was studied and the dissolution mechanism was discussed from the point of view of electrochemistry.

The dissolution rate in acid solutions obeyed a linear rate law and was expressed as $d[Cr^{3+}]/dt = k a_{H^+}^{0.56} \times a_{A^-}^{m}$, where a_{H^+} is the proton activity, a_{A^-} the anion activity and $m=0.29$ for SO_4^{2-} and $m=0.27$ for Cl^-.

The dissolution rate is determined by superimposing the following two coupling and coupled reactions whose rates depend upon the potential difference at the hydrous oxide-solution interface :

$$OH^-_{(H.O).} + H^+_{aq} \rightarrow H_2O_{aq}$$

$$[\text{chromium complex}]^{n+}_{(H.O.)} \rightarrow [\text{chromium complex}]^{n+}_{aq}$$

where H. O. denotes hydrous chromium oxide. An electrochemical dissolution mechanism is proposed which involves as an intermediate complex $CrSO_4^+$ for perchloric acid solutions containing SO_4^{2-}, $CrCl_2^+$ or $Cr(OH)Cl^+$ for those containing Cl^-, and $Cr(OH)_2^+$ for pure perchloric acid solutions. (English)

Dissolution of Hydrous Metal Oxides in Acid Solutions

M. Seo and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
24, 399 (1975), No. 8

The dissolution rate of hydrous oxides of iron, chromium and nickel in acid solutions was expressed as follows ; $v = k a_{\mathrm{H}^+}^{l} \times a_{m}^{\mathrm{A}}$, where a_{H^+} is the proton activity, a_{A} the anion activity, l the reaction order for proton and m the reaction order for anion. The value of l is close to 0.5 irrespective of the species of hydrous oxides but the value of m depends upon the anion species. The dissolution mechanism of hydrous oxide was discussed from electrochemical point of view. The dissolution reaction may be regarded as consisting of the following two coupling and coupled reactions.

$$\mathrm{OH}^{-}_{(\mathrm{H.O.})} + \mathrm{H}^{+}_{aq} \longrightarrow \mathrm{H_2O}_{aq}$$

$$[\mathrm{Me(OH)}_n(\mathrm{A}^{r-})_p]^{(z_+ - n - rp)+}_{(\mathrm{H.O.})} \longrightarrow [\mathrm{Me(OH)}_n(\mathrm{A}^{r-})_p]^{(z_+ - n - rp)+}_{aq}$$

where $[\mathrm{Me(OH)}_n(\mathrm{A}^{r-})_p]^{(z_+ - n - rp)+}$ represents the intermediate metal-anion complex transferring across the Helmholtz layer at the hydrous oxide-electrolyte interface. The rate of these two reactions is controlled by the potential difference, ϕ_{HL}, across the Helmholtz layer, and the net-dissolution rate of hydrous oxides can be determined by superimposing the polarization curves (potential difference, ϕ_{HL}, vs. reaction rate) of the two coupling and coupled reactions. The intermediate metal-anion complex has been estimated from the comparison of experimental results with theoretical derivation by assuming the Freundlich isotherm for the adsorption of anions on hydrous metal oxide. (English)

Membrane Potentials of Nickel Hydroxide Precipitate Membranes

M. Sakashita and N. Sato

Corrosion Engineering Boshoku Gijutsu),
24, 67 (1975), No. 2

Measurements of membrane potentials across nickel hydroxide precipitate membranes have been made to estimate the transport number of anions, the order of selectivity for anions, and the fixed charge concentration. The membranes show a high selectivity for anions; from the measurements of the membrane potentials, the transport number for anions evaluated to be 0.98 in sodium chloride, nitrate, perchlorate, and sulphate solutions. The order of the selectivity for anions determined with the biionic potentials is $OH^- > SO_4^{2-} > Br^- > I^- > Cl^- > NO_3^- > ClO_4^-$. This order of the selectivity is the same as that of the mobility in aqueous solutions, but the difference in the selectivity for these anions is greater in the membranes than in aqueous solutions. Nickel cations on nickel hydroxide precipitates constitute the fixed ion matrix characterizing the membranes as an anion exchanger, and its concentration is determined to be about 0.4 g equiv./liter by comparing the experimental membrane potentials with the theoretical values according to the fixed charge theory of membranes. (English)

Water Transference Through Nickel Hydroxide Precipitate Membrane

M. Sakashita and N. Sato

Electroanalytical Chemistry and Interfacial
Electrochemistry, **62**, 127 (1975)

The transference of water that results from ion migration through the nickel hydroxide precipitate membrane was studied in chloride, perchlorate, nitrate, and sulphate solutions to estimate the transference number of water and the co-ion transport. In the systems of univalent anions, the moles of water transported per mole of electrons in 0.1 *N* solutions is almost identical to the hydration number of each anion. This water flow decreases gradually as the concentration of external solution increases, because of increase in the co-ion (cation) transport with increasing concentration of the solution. In the system of sulphate solutions the co-ion transport is remarkable, the transport number of Na^+ ions being 0.03 in 0.01 *N*, 0.27 in 0.10 *N*, and 0.50 in 0.5 *N* Na_2SO_4 solution. This large co-ion transport in Na_2SO_4 solution is attributed to the partical replacement of hydroxyl groups on the membrane by SO_4^{2-} ions, which then acts as a negative fixed charge. The order of the selectivity for co-ion transport is $K^+ > Na^+ > Li^+ > Ni^{2+} \geqslant Mg^{2+}$ in sulphate solutions and also in chloride solutions, although the transport number of the cations is much smaller in chloride solution than in sulphate solution. (English)

Fundamental Studies on the Reaction between Metal Sulphides and Water Vapour at High Temperatures

R. Shibayama and T. Tanaka

Journal of the Mining and Metallurgical Institute
of Japan, **91**, 154 (1975) No. 1045

The reaction between ferrous sulphide and water vapour showed the evolution of hydrogen together with H_2S, due to the oxidation of ferrous iron to magnetite.

The effects of temperature and addition of lime to pyrrhotite, chalcopyrite, and bornite upon the evolution of hydrogen were examined.

Hydrogen evolution was accelerated by the addition of lime and the conversion of CaS to $CaSO_4$ was confirmed. Formation of magnetite layer around a core of high copper concentration was also observed during the oxidation of chalcopyrite and bornite by water vapour.

The core converted initially to bornite then to Cu_2S and finally to matallic copper. (Japanese)

A Study for Effective Utilization of Hydrogen Sulphide

H. Kiuchi and T. Tanaka

Journal of the Mining and Metallurgical Institute
of Japan, **91**, 155 (1975) No. 1045

The object of this study is to recover hydyogen from hydrogen sulphide which can be obtained from desulphurization process of petroleum, acid leaching of pyrrhotite and hydrogen reduction of metal sulphides.

Cyclic treatments of hydrogen sulphide by combination of following two reactions were carried out:

$$Pb(l) + H_2S \rightleftharpoons PbS(s) + H_2 \qquad (1)$$

$$PbS + O_2 \rightleftharpoons Pb(l) + SO_2 \qquad (2)$$

Hydrogen concentration above 80% was obtained at 800°C by one step blowing into molten lead.

The reaction (1) was enhanced by 1 wt.-% Ni addition to molten lead.

Oxidizing roasting of lead sulphide under reduced pressure or in an atmosphere of less than 1% oxygen concentration showed effective results for regeneration of lead metal from lead sulphide. (Japanese)

Hydrogen Economy from the Viewpoint of Nonferrous Extractive Metallurgy

T. Tanaka, R. Shibayama
and H. Kiuchi

Journal of Metals, Vol. 27, No. 12 (1975)

The viability of hydrogen as a secondary energy source has been watched in the field of energy industry, as well as electricity. For this reason, the so-called thermochemical process for water splitting, in which the heat from nuclear fission or solar energy is utilized directly to produce hydrogen and oxygen from water is being actively studied in many countries.

Considering this situation, the development of new techniques for metal smelting centered on hydrogen can be expected in the future.

This paper shows one path which may be taken in the future of sulphide ores smelting from the two fundamental points of view. (English)

Catalytic Activity and Exoelectron Emission of Solids

Norio Sato

Surface (HYOMEN), **13**, 221 (1975)

The author reviews the application of exoelectron emission to investigation of catalytic activity of solids. Exoelectron emission, the vaporization of very low energy electrons from solids, is very sensitive to the defect structure of solid surfaces, and therefore has been used as an effective tool for the study of solid catalysts. The article contains the method of exoelectron emission measurements, a variety of exoelectron emission from solids, the relation between surface detects and exoelectron emission, the relation between catalytic activity and exoelectron emission, the exoelectron emission and partial oxidation of ethylene on silver catalyst, and the exoelectron emission and CO oxidation on platinum catalyst. (Japanese)

Structure of Porous Vycor Glass and Its Adsorption Characteristics of Water

—— An Application of Positron Annihilation Method ——

Y. Ito, T. Yamashita and M. Nagasaka

Appl. Phys. **6**, 323 (1975)

Positron lifetimes in porous Vycor glass have been measured. There are four lifetime components, and the fourth component has been assigned to o-Ps annihilation in large pores of radius 34 Å. The intensity I_4 has been corrected to a specific surface area, but the value obtained from I_4 by the Monte Carlo method is smaller than that obtained by the BET method. From variations in (τ_4, I_4) against the kinetics of adsorption of water vapor, a rough picture of water adsorption is presented. (English)

Electron Emission from Vacuum Evaporated Tin-oxide Films

T. Hanasaka, T. Satake, M. Hashiba
and T. Yamashina

Proc. 6th Internl. Vacuum Congr. 1974, Japan.
J. Appl. Phys. Suppl. 2, Pt. 1, 277 (1174)

The cold emission characteristics of the vacuum evaporated tin-oxide films with various forms were investigated and both field and self-sustained emission up to 70 μA were obtained from most samples at anode valtage of about 400 volts. Self-sustained emission started without any primary electron bombardment and maintained itself for the duration of more than 100 hrs. Field emission acted as a trigger for the start of self-sustained emission.

Both emissions obtained from a neck formed in the films did not decrease with the decrease in neck size, while the emission efficiency seemed to slightly increase with it. Small neck was therefore desirable for obtaining high current density. The maximum current density obtained in this study was about 0.2 A/cm^2 for the neck size of 0.1 × 0.3mm. (English)

Methods of Measurement of Adsroption and Catalysis by Solid Surfaces with Small Surface Area

K. Watanabe and T. Tamashina

Asahi Garasu Kogyo Shoreikai Kenkyu
Hokoku **25**, 253 (1974)

The apparatus for studies on catalysis and adsorption by clean solid surfaces were constructed and examined. The apparatus are such as a xenon adsorption system for measuring small surface areas, a high sensitive Pirani gauge with no pumping action for active gases and an adsorption measuring system of active gases at very low pressures and an apparatus for measuring the rate of catalytic reaction at very low pressures.

It was capable to determine the surface area of 8～500 cm^2 within only 30 to 60 minutes which were about 1/5 of the measuring time by the other xenon adsorption methods. By using our high sensitive Pirani gauge, pressure of active gases in the range of 10^{-7}～10^{-2} Torr could be detectable. The calibration curves for several kinds of active gases showed remarkably good linearity in the pressure range mentioned above. In addition the gauge showed high stability at least for two months.

It was also capable to determine very easily the rate of catalytic reaction under very low pressures. An example was presented on the measurement of hydrogen-deuterium equilibration reaction on nickel evaporated films with sur face area about 400 cm^2 at 10^{-6}～10^{-3} Torr by a flow method.

This paper will describe these apparatus in detail with some applications to the catalysis studies. (Japanese)

A Study of Catalytic Activity Factors on Clean Surface of Copper-Nickel Alloys

Y. Takasu and T. Yamashina

Proc. 2nd Internl. Conf. on Solid Surfaces,
1974, Japan. J. Appl. Phys. Suppl.
2, Pt. 2, 493 (1974)

The relation between catalytic activity to the hydrogen-deuterium exchange reaction as well as work function and alloy composition of clean surface of copper-nickel alloys was studied. Clean surface of alloys was prepared by argon ion-beam bombardment and annealing, and the surface composition of alloys was determined by an Auger spectroscopy. The catalytic activity was found to be greatest in pure nickel and then to decrease continuously as copper content in the alloys increases. The catalytic activity $K_m(X)$ could be expressed by an equation.

$$\log K_m(X) = aX + b,$$

where X is nickel content in the alloys and a and b are constants, while the work function Φ of copper-nickel alloys changed linearly with their alloy composition, i. e.,

$$\Phi(X) = cX + d (c \text{ and } d\text{: constants}).$$

The catalytic activity factors in copper-nickel alloys were discussed on the bases of electronic structure and behaviours of hydrogen adsorption which have been presented by several workers.
(English)

Preparation of Titanium Oxide and Nitride Films by means of Reactive Sputtering

T. Abe and T. Yamashina

J. Vacuum Society of Japan **18**, 375 (1975)

Titanium oxide and nitride films containing various amount of oxygen and nitrogen have been prepared by means of reactive sputtering method. Changing the partial pressure of oxygen and nitrogen from 5×10^{-7} to 5×10^{-3} Torr in argon gas (total pressure was maintained at 5×10^{-3} Torr), the deposition rate, electrical resistivity, structure and chemical composition of sputtered films have been observed.

When the partial pressures of oxygen and nitrogen in the sputtered gas were increased, the deposition rate of films began to decrease drastically at the specific partial pressures. In particular, two limiting pressures at which the deposition rates changed drastically were observed to exist in the case of titanium-nitrogen sputtering system. The electrical resistivity of the films also began to change rapidly at the same limiting pressures. In the X-ray diffraction analysis, it was found that TiO and TiN appeared suddenly in the sputtered films at the specific pressures of reactive gases.

The ultimate analysis of the sputtered films also have been made by means of the sputter-etching technique and Auger electron spectroscopy.

On the basis of the experimental data, discussion was made on the deposition rate of the films by applying our theretical model. (Japanese)

The Deposition Rate of Metallic Thin Films in the Reactive Sputtering Process

T. Abe and T. Yamashina

Thin Solid Films **30**, 19 (1975)

A model is presented giving the deposition rate during the reactive sputtering of metals in atmospheres of oxygen and nitrogen in an argon plasma. On the basis of the difference between the sputtering rates of the metal and its chemical compound, the surface coverage, the sticking probability and the incident flux of reactive gas atoms, a semi-empirical equation has been derived. Computer calculations have been made to determine the specific constant values for several reactive sputtering processes such as Mo–O_2, Mo–N_2, TiO_2 and Ti–N_2. In each experimental observation an abrupt decrease of the sputtering rate was found at a particular pressure of reactive gas.

The model might be applied successfully for sputtering processes over a wide pressure range of the reactive gas. (Engilsh)

Gettering Rate of Hydrogen and Deuterium by Titanium and Zirconium at Elevated Temperature

M. Nagasaka and T. Yamashina

Proc. 6th Internl. Vacuum Congr. 1974, Japan. J.
Appl. Phys. Suppl. 2, Pt. 1, 61 (1974)

The gettering rates of hydrogen and deuterium at pressures of 10^{-4}–10^{-2} Torr by titanium and zirconium were studied in the temperature range 500–700°C, by means of a volumetric method. The gettering rates were kept constant in the initial period of reaction, which showed the linear sorption to be controlled by the reaction at the gas-solid interface. In the latter period, the rate began to decrease according to the increment of hydrogen concentration in solid, and finally became zero when the concentration attained to equilibrium value. It was also found that the gettering rate of hydrogen is about twice faster than that of deuterium under the same condition in both cases of titanium and zirconium. (English)

Activation Analysis with a 45 MeV Electron Linear Accelerator

T. Morozumi, H. Narita and H. Ohashi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 78, 119 (1975)

Activation analysis of several materials was performed with the Hokkaido University 45 MeV Electron Linear Accelerator. The combination of a lead target and a paraffine moderator was utilized to produce the thermal neutron for the radio-activation. Sixteen samples of metallic and inorganic materials were irradiated, and the γ-ray spectra were measured with a well-type NaI(Tl) scintillation counter. In all cases, the build-up curves of each activated nuclideds were given fairly well by the modified exponential formula. Since the neutron flux produced by the linear accelerator is very low in comparison with that of a nuclear reactor, remarkable activation was obtained for a limited number of nuclides which had high activation cross section and/or short half lives. However, rather high sensitivity and accuracy were obtained in the quantitative analysis of some elements in practical materials such as hafnium in zirconium metals, manganese in iron, steels and iron compounds, and molybudenum and other elements in austenitic stainless steels. (Japanese)