ANNUAL REPORT

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CORROSION RESEARCH

published by

THE CORROSION RESEARCH GROUP

FACULTY OF ENGINEERING
HOKKAIDO UNIVERSITY

NO. 2 DECEMBER 1973

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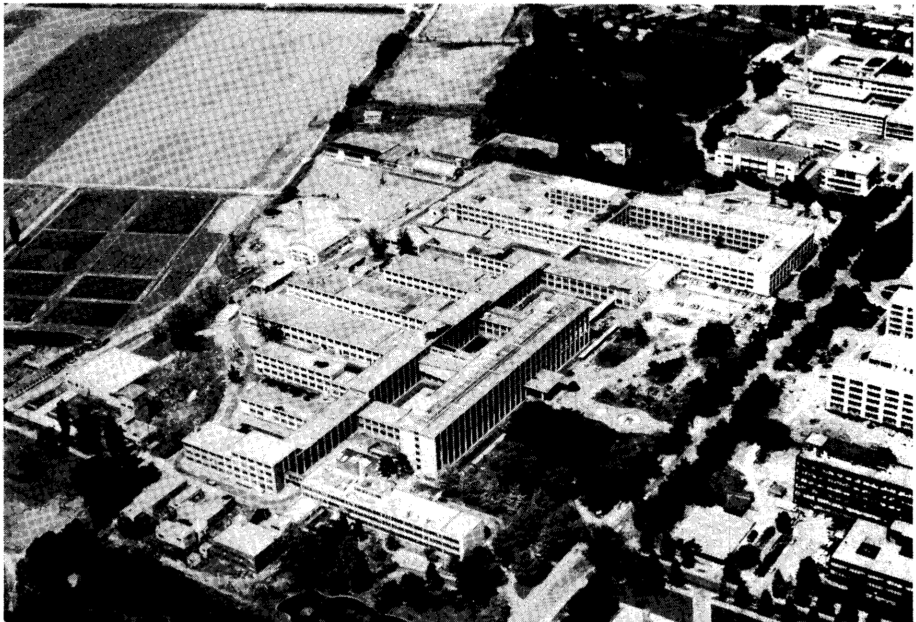

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HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

T. Yamauchi, N. Oya, H. Murohashi, T. Tani,
A. Matsui, T. Inugai, H. Hagiwara, T. Otsubo,
T. Saito, R. Maruyama and U. Yonezawa

This laboratory is investigating the dry corrosion (oxidation and sulfurization) of metals and alloys. The diffusion in metals and alloys are also being investigated by means of solid couple and metallic vapor techniques. Furthermore, the decomposition of metal carbides in a wet atmosphere at room temperature and the hydration of magnesia made from dunite are being studied.

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

(1) Kinetics of oxidation of Co and Ni based alloys; All these kinetics are checked by comparing their behaviors with the postulates from Wagner's new theory and the development of the theory by Dalvi et al.

(2) Mutual diffusion in Fe sulfide-Ni sulfide system; In order to clarify the diffusion behavior an FeS–NiS diffusion couple is investigated at 600–800°C and the mutual diffusion coefficients are determined.

(3) Metallizing of refractory metals and oxidation prevention; Ta metal is calorized by use of Al vapor from Fe–Al powdered alloy ($FeAl_2$) at 1000°C for various times and then the treated metal sheets are oxidized in air at 1000–1200°C. At high temperatures calorized Ta is rather protective against oxidation.

Oral presentations

Mechanism of Ferrous Sulfide Scale Growth; T. Narita and K. Nishida: The 8th Annual Meeting of Corrosion Research Association in Hokkaido, Feb. 1973.

Self-diffusivity of Nickel in the Ferrous Sulfide formed on Iron based Nickel Alloys ; T. Narita and K. Nishida : The Spring Meeting of the Japan Institute of Metals, April 1973.

On the Study of Cation Distribution in the (Co, Ni) O Scale (II)-Alloying Composition Dependence of Ni and Co Distributions ; T. Narita, N. Ohya and K. Nishida : *ibid.*, April 1973.

On the Growth of Multi-Layer Sulfide Scale formed on Fe–Cr alloys ; T. Inugai, T. Narita and K. Nishida : The Hokkaido Section Meeting of Japan Institute of Metals and Iron and Steel Institute of Japan, July 1973.

Interdiffusion in the Fe–Sb Alloy System ; H. Murohashi and K. Nishida : *ibid.*, July 1973.

Atomic Number Effect on the Cation Distribution in Ferrous Sulfide Scale ; T. Narita and K. Nishida : The 40th Annual Meeting of the Japan Electrochemical Society, Aug., 1973.

Alloying Element Effect on Sulfurization Rate and Scale Morphology of Fe based Alloys ; T. Narita and K. Nishida : *ibid.*, Aug., 1973.

Recent Studies on the Multi-phase Diffusion —Based on the Formation of Diffusion Coating Layer— ; K. Nishida : The 1st Symposium on Diffusion phenomena (Japan Inst. Metals), July, 1973.

Analysis of Sulfide Scale Formed on Fe–Mn Alloys; K. Nishida, G. Sasaki, and T. Narita : The 20th Annual Symposium on Corrosion and Protection, July, 1973.

Analysis of Multi-layer Sulfide Scale formed on Fe–Cr Alloys ; T. Narita, K. Inugai, and K. Nishida : The Fall Meeting of Japan Institute of Metals, Oct., 1973.

Interdiffusion in Fe–Sb Alloys (I) ; K. Nishida and H. Murohashi ; *ibid.*, Oct., 1973.

Distribution of Cation in the Oxide Scale and Alloying Elements in the Alloy Substrate during High-temperature Oxidation of Ni–Co alloys ; T. Yamauchi, T. Narita and K. Nishida : The Hokkaido Section Meeting of Japan Institute of Metals and Iron and Steel Institute of Japan, Nov., 1973.

On the Distribution of Ni in the Oxide Scale formed on a Co–0.45 wt% Ni Alloy at Elevated Temperature ; K. Nishida, T. Narita, and N. Ohya : The International Colloquium on Materials Science in Cracow (Poland), Nov., 1973.

Hydrolysis of Mn–C–Fe Ternary Alloys with Water Vapor ; K. Atarashiya : The Spring Annual Meeting of Japan Institute of Metals, April 1973.

Properties and Usages of Magnesia made from Dunite with Dry Method ; K. Atarashiya : The 3rd Symposium on Mettallurgy of the Hokkaido Section of Japan Institute of Mining and Metallurgical Engineering, Nov., 1972.

NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. T. Morozumi, Assist. Prof. H. Ohashi,
Mr. T. Mizuno, Mr. K. Hirohara
and Miss N. Koreyasu

Students

M. Kosuge, M. Koizumi, H. Gotoh, K. Fujinaga,
H. Narita, S. Hayashi, T. Isogawa, T. Suzuki,
T. Funakoshi, M. Nishida and Y. Kawaguchi

This laboratory is investigating physico-chemical and electrochemical problems in the fields of nuclear fuels and reactor materials engineering. Our main concerns of corrosion problems are the corrosion of metallic reactor materials and the application of nuclear chemical methods to the corrosion researches. The oxidation and the dissolusion of the ceramic nuclear fuels are also investigated on the background of corrosion studies.

Topics of our recent researches are listed as follows:

(1) Dissolution of zirconium in aqueous fluoride solutions. Among various factors investigated, pH of the solution was found to be most essential for the occurance of the auto-oscillation of corrosion potential. This experimental finding was explained thermodynamically by using the pH-potential diagram of $Zr–F^-–H_2O$ system. A. C. impedance-frequency characteristics were measured at several phases of the periodic change of corrosion potential.

(2) Hydrogen uptake into zirconium and titanium. The rate of hydogen uptake into these metals, which is accompanied with corrosion and electrochemical polarization, is measured by using the nuclear chemical method and the vacuum technique. The former method is applied to measure the growth rate of hydride layer of thickness less than 10,000 Å, and the latter method to more than 10,000 Å. The variations of the rate law were observed in accordance with the experimental coditions and also the thickness of hydride layer.

(3) Application of Mössbauer measurement to oxidation of iron in air. Mössbauer absorption spectra of tarnished iron foils, which were oxidized in air for various time durations at various temperatures between 300 and 600°C, were measured. By analysis of the spectra data, the growth rates of the layers of the intermediate Fe_3O_4 and the final product Fe_2O_3 were obtained.

(4) Measurement of Mössbauer spectra of iron oxides and hydroxides. Variuos kinds of iron oxides and hydroxides were synthesized and the Mössbauer spectra of these compounds were measured. The changes of chemical reactivities to several aqueous redox reagents by thermal treatment of these compounds were also measured and correlated with the informations from the Mössbauer measurements.

(5) Oxidation of uranium dioxide. The effects of the rising rate of temperature during the initial oxidation from UO_2 to U_3O_7 and the time duration of annealing of the intermediate U_3O_7 on the rate of subsequent oxidation from U_3O_7 to U_3O_8 were investigated by a thermogravitational balance of Gulbransen type.

(6) Effect of post-irradiation on the rate of corrosion of pure aluminium in sodium chloride solution. Corrosion rates of the commercially purest and the zone-refined aluminium were measured at various constant pHs by using the electrochemical pH-stat. The effect of the post-irradiation (10^{20} nvt) in Japan Material Testing Reactor was investigated.

Oral Presentations

Effect of Thermal History on the Oxidation of Uranium Dioxide; H. Ohashi, E. Noda and T. Morozumi: The 8th Annual Meeting of Corrosion Research Association in Hokkaido. Feb. 1973.

Auto-oscillation of Corrosion Potential of Zirconium; M. Moriya and T. Morozumi: *ibid.*, Feb. 1973.

Oxidation of Uranium Dioxide; H. Ohashi, E. Noda and T. Morozumi: Annual Meeting of the Atomic Energy Society of Japan, March 1973.

Measurement of Stopping Power of Metallic Heavy Hydrides

Against 10 to 100 KeV Deuteron by *dn*-Reaction Method ; T. Mizuno and T. Morozumi : Annual Meeting of the Atomic Energy Society of Japan, March 1973.

Measurement of Growth Rate of Hydride layers on Zirconium and Titanium by Nuclear-chemical *dn*-Reaction Method ; T. Mizuno, T. Suzuki and T. Morozumi : The 1973 Joint Meeting of the Hokkaido Branches of Japan Chemical Society and Japan Society of Analytical Chemistry, Feb. 1973.

Rate Laws of Growth of Hydride Layers on Zr and Ti ; T. Morozumi, T. Mizuno and T. Suzuki : The 20th Symposium on Corrosion and Corrosion Prevention in Japan, May 1973.

Effect of pH on the Corrosion Potential Oscillation of Zirconium ; T. Morozumi M. Moriya and M. Mizuno : The 20th Symposium on Corrosion and Corrosion Prevention in Japan, May 1973.

Kinetic Studies on Electrochemical Growth of Hydride Layers on Zirconium and Titanium Surfaces ; T. Mizuno and T. Morozumi : The 40th Meeting of Electrochemical, Society of Japan, Aug. 1973.

Electrode Impedance Change Accompanied with Oscillation of Corrosion Potential of Zirconium in NH_4F Solution ; T. Morozumi, M. Moriya and T. Hirota : The 40th Meeting of Electrochemical Society of Japan, Aug. 1973.

Exoelectron emission ; H. Ohashi : The Meeting of Thin Film and Surface Physics Section of Japan Applied Physics Society, Dec. 1973.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Dr. H. Takahashi,
Mr. H. Tamura, Mr. Y. Otake
and Miss K. Adachi

Students

H. Konno, K. Takahashi, M. Koda, Y. Sato,
H. Matsuyoshi and Y. Shibata

Research being made in this laboratory is mainly connected to the hydrolytic dissociation of metallic ions in aqueous solutions and to the mechanism of anodic oxidation of metals in aqueous solutions. Investigations are carried out also on the inorganic corrosion inhibitors, the mechanism of plating reactions and the methods of analyses of metal ions in various environments.

Topics of present research are as follows:

(1) The formation and dissolution of porous anodic oxide films on aluminum. Dissolution behavior of oxide during anodizing and on open-circuit have been examined in various acid electrolytes as a function of anodizing voltage. An ultra-thin sectioning technique is being developed for electronmicroscopic examination of films. Distributions of electrolyte anions and protons in the film were determined by using a stepwise dissolution technique in a suitable solution.

(2) Pore-filling phenomenon, observed when aluminum specimen covered with porous anodic oxide films is anodized in a neutral borate solution, has been examined to determine the transport numbers of Al^{3+} and O^{2-} in the oxide.

(3) Deposition of copper from Cu-pyrophosphate solutions. The cathodic polarization characteristics of copper has been examined as functions of the temperature, the solution composition and pH, the rotating disk electrode technique being used. The behavior of adsorption of pyrophosphate ions on the surface of the specimen is investigated to clarify the mechanism of the plating reaction.

Similar type of investigation is being conducted for copper deposition from cyanide solutions.

(4) Estimation of corrosion rate by the measurement of polarization resistance. Method of measuring the polarization using a constant current and the method of constructing the calibration curve have been developed to obtain the relationship between the corrosion rate and the polarization resistance. Application of this method to the evaluation of corrosion inhibitors is being made with success.

(5) Air-oxidation of ferrous ion in neutral solution. Oxidation rate is being measured as functions of the concentrations of ferrous ions, oxygen pressure and pH of the solution. Effect of the nature and the concentration of electrolyte anions and the effect of ferric hydroxide are taken into consideration.

(6) Method of analysis of ferric ions in aqueous solution is being investigated with intention to differenciate the amount of mononuclear species from that of the polynuclear spiecies. The fractions of these spiecies is found to change with the solution pH and the concentrations of co-existing complexing agents.

Oral Presentations :

Coprecipitation of Cd^{2+} Ions with Aluminum Hydroxide—Effect of Coexisting Substances ; K. Goto, H. Tamura, A. Koike and M. Nagayama : The 1973 Winter Meeting of the Hokkaido Sections of the Japan Anal. Chem. Soc. and the Japan Chem. Soc., Feb. 1973.

Determination of Al Ions Using Ferron and Surface Active Agent —Masking of Diverse Ions ; K. Goto, H. Tamura, T. Maekawa and M. Nagayama : *ibid.*, Feb. 1973.

Distributions of Anions and Protons in Porous Anodic Oxide Films on Al ; H. Takahashi and M. Nagayama : The 8th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb. 1973.

Sealing Reaction of Porous Anodic Oxide Films on Al ; H. Takahashi, K. Fujioka K. Goto and M. Nagayama : *ibid.*, Feb. 1973.

Structural Change of Porous Anodic Oxide Films on Al with Forming Voltage; H. Takahashi and M. Nagayama: *ibid.* Feb. 1973.

Spectrophotometric Determination of Al Ions Using Ferron and Tertially Ammonium Salt; K. Goto, H. Tamura and M. Nagayama: The 28th Annual Meeting of the Japan Chem. Soc., Apr. 1973.

Air-Oxidation of Ferrous Ion in Aqueous Solution; H. Tamura. K. Goto and M. Nagayama: Ibid., Apr. 1973.

Mechanism of Sealing Reaction of Porous Anodic Oxide Films on Al; H. Takahashi, K. Yamada, K. Goto and M. Nagayama: *ibid.*, Apr. 1973.

Composition of Porous Anodic Oxide Films on Al and Mechanism of Their Formation; M. Nagayama and H. Takahashi: The 20th Symposium on Corrosion and Corrosion Prevention in Japan, May 1973.

Cathodic Polarization Characteristics of Rotating Copper Disk Electrode in Cu-Pyrophosphate Solutions; H. Konno and M. Nagayama: *ibid.*, May 1973.

Structures of Porous Anodic Oxide Films on Al and Behavior of their Sealing Reactions; H. Takahashi, M. Nagayama, K. Yamada and K. Fujioka: The 1973 Spring Meeting of the Metal Finishing Soc. Japan, May 1973.

Study of Porous Anodic Oxide Film on Al by Ultra-Thin Sectioning Technique. —Behavior of Film Growth at Initial Periods of Anodizing; M. Nagayama, H. Takahashi, H. Akahori and A. Kitahara: The 20th Annual Meeting of the Japan Soc. for Electronmicroscopy, May 1973.

Determination of Anion Distributions in Porous Anodic Oxide Films; H. Takahashi, K. Goto and M. Nagayama: The 34th Symposium on Analytical Chemistry, July 1973.

Formation of Al-Ferron Complexes in the Presence of Tertially Ammonium Salt; K. Goto, H. Tamura and M. Nagayama: *ibid.*, July 1973.

Effect of Formation Voltage on Distribution of Electrolyte Anions in Porous Anodic Oxide Films on Alumininum ; H. Takahashi and M. Nagayama : The 40th Annual Meeting of Japan Electrochem. Soc., Aug. 1973.

Mechanism of Electrodeposition of Cu from Cu-Pyrophosphate Solution ; H. Konno, K. Goto and M. Nagayama : *ibid.*, Aug, 1973.

Electronmicroscopy of Porous Anodic Oxide Films on Al by the Aid of an Ultramicrotome Technique. —Open-Circuit Dissolution Behavior of the Film ; H. Takahashi, M. Nagayama and H. Akahori : Congress on Electronmicroscopy (sponsered by Belgian, German and Netherlandish Societies for Electronmicroscopy), Sept. 1973.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

K. Igarashi, H. Iizawa, T. Mikami, T. Nagasawa,
Y. Sakaba, S. Sato, M. Takada and S. Watanabe.

Activities of this laboratory are concerned mainly with properties and failures of metals in service of machine. Some projects of research are listed as follows :

(1) Growth mechanism of grey cast iron ; A diffusion porosity theory for the growth proposed by Dr. K. Nagaoka has been confirmed experimentally by dilatometer tests and scanning-electron-microscopic observations. Effects of the heating atmosphere on the growth were tested with fruitful results.

(2) Strength of cast iron ; Fracture strength of beam and notched bar made of cast iron was studied by means of analysing the stress near the bending surface and at the notch root.

(3) Failure analysis of machine members ; Causes of machine accidents practically occurred were investigated with metallurgical and mechanical analysis. Recently, SEM fractographic examinations are being applied to failure analysis.

Oral Presentations

On the Bending Fracture Strength of Steel at the Liquid Nitrogen Temperature ; T. Noguchi : The 22nd Grand Lecture Meeting of The Society of Material Science, Japan, May 1973.

On the Rupture Strength of Deep-notched Cast Iron ; T. Noguchi and K. Nagaoka : The 83rd Grand Lecture Meeting of The Japan Foundrymen's Society, May 1973.

Accelerating Effects of Atmosphere on the Growth of Cast Iron ; M. Sōma and K. Nagaoka : The 83rd Grand Lecture Meeting of The Japan Foundrymen's Society, May 1973.

CURRENT ACTIVITIES

A Simplified Formula for the Bending Strength of Cast Iron ; T. Noguchi and K. Nagaoka : The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1973.

Effects of Graphite Form on the Growth of Cast Iron ; M. Sōma and K. Nagaoka : The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1973.

Effects of Atmospheres on the Growth of Cast Iron ; M. Sōma and K. Nagaoka : The 84th Grand Lecture Meeting of The Japan Foundrymen's Society, Oct. 1973.

ELECTROCHEMISTRY LABORATORY

Prof. Dr. N. Sato, Assist. Prof. Dr. K. Kudo,
Dr. M. Seo, Mr. M. Sakashita, Miss C. Miura
and Dr. M. I. Ismail*

Students

T. Otsuka, R. Nishimura, Y. Otake, N. Arayama,
R. Saito, and R. Taira

Investigations of the passivity of iron-group metals and alloys in aqueous solution make up at present the main work of this laboratory. Studies of the composition and structure of anodic passivation films formed on iron, nickel, cobalt, chromium, and iron-nickel alloys are continuing by use of electrochemical and ellipsometric techniques. Two ellipsometers, mannual and automatic, are now in operation and two others are being set up for ellipsometric spectroscopy and micro-ellipsometry.

Beside passivity work, studies of high temperature oxidation of iron in contaminated oxygen gasses are being carried out to see the effect of SO_2, CO_2 and H_2O, on the oxidation kinetics and oxide layer structures. Three vacuum-microbalances of different sensitivities and a scanning electron-microscopy have been used for this series of studies.

Furthermore, a program of membrance work with hydrous nickel oxide membrances is under way nearing completion. An extension of this type of investigations with other metal oxide membranes is projected.

Dr. Kudo is staying abroad at professor Winterbottom's laboratory, the Technical Institute of Trondheim, Norway, for one year from October 1973, and Dr. Seo at professor Staehle's laboratory, the Ohio State University, U.S.A., for two years from October 1972.

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* JSPS Research Fellow from the Faculty of Engineering, Alexandria University, Alexandria, Egypt.

CURRENT ACTIVITIES

Professor Sato attended with a paper of iron passivity the Fifth European Congress of Corrosion, 24–28 September 1973, at Paris by order of the Japan Science Council, and visited the Central Institute of Chemical Metallurgy of C.N.R.S. at Vitry-sur-Seine in France, Professor Amsel's laboratory (Solid State Physics) of C.N.R.S. at Paris in France, Professor Epelboin's laboratories (Electrochemistry) of C.N.R.S. at Paris in France, Prafessor Vetter's laboratory (Electrochemistry) of the Institute of Physical Chemistry at Free University of Berlin in Germany, and Professor Bianchi's laboratory of the University of Milano in Italy.

Oral Presentation

Anodic Oxide Films on Iron in a Neutral Solution; K. Kudo, N. Sato and T. Noda: The 8th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1973.

Growth Kinetics of the Passivation Films in Phosphoric Acid Solutions; T. Noda, K. Kudo and N. Sato: *ibid.*, Feb., 1973.

Passive Films on Cobalt; T. Otsuka, M. Sakashita, K. Kudo and N. Sato: *ibid.*, Feb., 1973.

Surfaces Passivation Films on Iron in a Neutral Solution; N. Sato and T. Noda: The Spring Meeting of the Japan Institute of Metals, Apr., 1973.

Ellipsometric Studies of Passive Oxide Films on Iron; N. Sato, K. Kudo and T. Noda: The 20th Annual Symposium on Corrosion and Protection, May 1973.

Passive Films on Iron-Nickel Alloys in a Neutral Solution; Y. Otake, K. Kudo and N. Sato: *ibid.*, May, 1973.

The Passivation Films on Iron in Acidic and Alkaline Solutions; T. Noda, K. Kudo and N. Sato: *ibid.*, May, 1973.

Ion Transport through a Hydrous Nickel Oxide Membrane; M. Sakashita and N. Sato: *ibid.*, May, 1973.

The Composition of Anodic Oxide Films on Cobalt in Slightly Alkaline Solution; T. Otsuka and N. Sato: Hokkaido Section Meeting of J.I.M. and I.S.I.J., July, 1973.

Anodic Oxidation of Cobalt; T. Otsuka, M. Sakashita, K. Kudo and N. Sato : The 40th Annual Meeting of the Japan Electrochemical Society, Aug., 1073.

Anodic Dissolution of Iron ; N. Sato, K. Kudo and T. Noda : *ibid.*, Aug., 1973.

Anodic Benaviour of Iron-Nickel Alloys ; Y. Otake, N. Sato, and K. Kudo : *ibid.*, Ang., 1973.

Selective Ion Transport through a Hydrous Nickel Oxide Membrane ; M. Sakashita and N. Sato : *ibid.*, Aug., 1973.

Anodic Dissolution of Metals ; N. Sato : Hokkaido Section Seminar of J.I.M., Aug., 1973.

Layer Structure of the Passivation Film on Iron in Acidic and Basic Solutions ; N. Sato and T. Noda : 5th European Gongress of Corrosion, Sept., 1973.

The Passivity of Iron in Aqueous Solution ; N. Sato : Invited Lecture at University of Paris, Groupe de Physique des Solides de L'E.N.S., Sept., 1973.

The Anodic Passivity of Iron, Nickel, Cobalt, and Iron-Nickel Alloys in Aqueous Solution ; N. Sato : Invited Lecture at the Free University of Berlin, Oct., 1973.

Ellipsometry in Corrosion Research ; K. Kudo, N. Sato and G. Okamoto : Commemoranive Lecture for a Corrosion Prevention Prize of the Committee of Preventing Corrosion in the JSPS, Dec., 1973.

ELECTROMETALLURGY LABORATORY

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

Students

M. Asakawa, T. Matsuda, Y. Karikome, K. Sato,
Y. Kawahara, H. Kim, M. Konno, N. Nishimae
and J. Sagawa

Research subjects in this laboratory are as followed:

(1) The structure and property of molten salt mixtures of aluminum chloride and alkali chloride are being estimated from the data of vapour pressure, equilibrium potential, transference number, and electrolytic conductance of these melts. The mechanism of anodic dissolution and cathodic deposition of aluminum in these molten salt mixtures is being clarified using rotating cylindrical electrodes by means of chronoamperometry, chemical analysis, and surface observation *in situ*. Laboratory scale tests for electrorefining and electrowinning of aluminum are also being carried out in these melts.

(2) Electrodeposition of iron and hydrogen in acidic ferrous sulphate solution containing a metallic or metalloid ion, which functions to poison the hydrogen evolution, is being studied by means of coulometry and chemical analysis. Fundamental studies of high speed electrorefining of copper are also in progress.

(3) Anodic dissolution and passivation of metals, mainly iron base alloys, are being investigated in molten alkali nitrates and nitrites by using potentiostatic, galvanostatic, and potential sweep methods. Corrosion tests in the melts are also carried out to compare with the data obtained by electrochemical techniques.

(4) The corrosion rates of iron, steel and copper under various heat transfer conditions are being determined at various temperatures by colourmetric analysis. Electrochemical measurements are also being carried out under these conditions. Effects of heat

transfer on pitting corrosion behaviour of stainless steel are being clarified in ferric chloride solutions.

Oral Presentation

Anodic Behaviour of Copper in Molten Alkali Nitrates ; T. Notoya, T. Ishikawa and R. Midorikawa : Hokkaido Section Meeting of Japan Chemical Society, Feb. 1973.

Influence of Inhibitor and Anionic Species on Temperature Change and Heat Transfer Effect of Corrosion Rate of Pure Iron ; T. Ishikawa and R. Midorikawa : The 8th Annual Meeting of the Corrosion Reseach Association in Hokkaido, Feb. 1973.

Fundamental Study on Metallic Corrosion under Boiling Heat Transfer Conditions ; S. Ohkubo, T. Ishikawa and R. Midorikawa : *ibid.*, Feb. 1973.

On the Anodic Passivation and Dissolution of Copper in Molten Alkali Nitrate and Nitrite ; T. Notoya, T. Ishikawa and R. Midorikaw : *ibid.*, Feb. 1973.

On the Corrosion Behaviour of Copper in Molten Alkali Nitrates and Nitrites ; T. Notoya, T. Ishikawa and R. Midorikawa : The 28th Annual Meeting of Japan Chemical Society, April 1973.

Temperature Change and Heat Transfer Effect of Corrosion Rate under Boiling Conditions ; S. Ohkubo, T. Ishikawa and R. Midorikawa : The 20th Symposium of Corrosion and Corrosion Prevention in Japan, May 1973.

Heat Transfer Effects on Corrosion Reaction controlled by Reaction Process ; T. Ishikawa and R. Midorikawa : *ibid.*, May 1973.

On the Cathodic Processes in Molten Alkali Nitrates ; T. Notoya and R. Midorikawa : Hokkaido Section Meeting of the Japan Chemical Society, July 1973.

Surface Preperation of Stainless Steel Specimen for Electrochemical Measurement ; T. Shibata and T. Ishikawa : The Meeting of Stainless Steel Subcommittee, 97th Comittee of Preventing Corrosion, The Japan Society for the Promotion of Science, July 1973.

Application of Rapid Polalization Measurement Method to Heat Transfer Corrosion of Pure Iron ; S. Isagoda, T. Ishikawa and R. Midorikawa : The 40th Annual Meeting of the Electrochemical Society of Japan, Aug. 1973.

Transference Nnmber of Various Ionic Species in Molten $AlCl_3$–NaCl Mixtures ; K. Sato, T. Sato, T. Ishikawa and R. Midorikawa : *ibid.*, Aug. 1973.

Anodic Behaviour of Cu and Cu–Ni alloys in Molten Alkali Nitrate and Nitrite ; T. Notoya : *ibid.*, Aug. 1973.

Kinetics of Electron Transfer Step of Hydrogen Evolution reaction on Gold in Sulphuric Acid ; T. Sasaki and A. Matsuda : *ibid.*, Aug. 1973.

A rule of Kinetics on Electron Transfer Process of Hydrogen Electrode Reaction ; A. Matsuda, R. Notoya, T. Ohmori, T. Sasaki and K. Kunimatsu : *ibid.*, Aug. 1973.

Transference Number of Various Ions in the Molten Salt Mixtures of Aluminum Chloride and Sodium Chloride ; T. Sato, T. Ishikawa and R. Midorikawa : The 7th Symposium on Molten Salt Chemistry, Nov. 1973.

NONFERROUS EXTRACTION METALLURGY LABORATORY

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

Students

S. Katagiri, K. Harashima, J. Iwahara, S. Katagiri,
S. Minami, M. Nakamura and K. Uehara

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

(1) Pyrometallurgy

i) Reduction kinetios 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 electronmicroscope, phenomenological comparison between the sulfidation and the reduction, effects of impurities on the rate of reduction, and measurements of the reduction rate of volatile metal sulphides are being made.

ii) Reaction between metal sulphides and water vapour at high temperatures : Thermodnamic and kinetic investigations are being made in connection with the production of hydrogen from sulphide ores.

(2) Hydrometallurgy

Electrochemical measurements in some pressure hydrometallurgy : The reaction kinetics of the oxygen pressure leaching of sulphide minerals and the hydrogan 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 temperatures up to 200°C and pressures of 50 kg/cm^2.

CURRENT ACTIVITIES

Oral Presentations

An Electrochemical Aspects on Pressure Precipitation of Nickel; T. Nagai and M. Sato: 2nd International Symposium on Hydrometallurgy, AIME, Chicago, Feb. 1973.

Direct Reduction of Lead Sulphide by Hydrogen; H. Kiuchi, M. Izumimoto and T. Tanaka: Annual Meeting of the Mining and Metallurgical Institute of Japan, Tokyo, Mar. 1973.

Thermal Decomposition of Copper Concentrate; R. Shibayama and T. Tanaka: *ibid.*, Mar. 1973.

On the Hydrogen Reduction of Cobalt Sulphides; R. Shibayama, S. Katagiri and T. Tanaka: Annual Meeting of Japan Institute of Metals, Fukuoka, Oct. 1973.

Pretreatment of Copper Concentrates by Hydrogen; R. Shibayama, S. Katagiri and T. Tanaka: Fall Meeting of Hokkaido Branch, The Mining and Metallurgical Institute of Japan, Nov. 1973.

Etch Figures on pyrite by Pressure Leaching; T. Nagai and H. Kiuchi: *ibid.*, Nov. 1973

VACUUM SCIENCE LABORATORY

Prof. Dr. T. Yamashina, Mr. K. Watanabe, Mr. M. Nagasaka,
Dr. S. Tanaka, Mr. M. Hashiba, Mrs. Y. Hirohata
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Students

T. Abe, K. Kumazawa, T. Sasaki,
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In this laboratory, research work on the reactivity of solid surfaces and vacuum engineering is in progress with the following subjects :

(1) Relation between catalytic activity and surface composition of clean surface of copper-nickel alloys : The structure and property of active sites on the alloys are investigated by using ultrahigh vacuum apparatus for catalytic measurement, Auger electron spectroscopy, and work function measurement.

(2) Effect of argon ion bombardment on the adsorption and catalysis of evaporated nickel and iron films : Clean films of nickel and iron are ion-bombarded with argon. To clarify the nature of active sites, the adsorption of hydrogen and nitrogen, and the catalytic activity for the isotopic exchange reactions of hydrogen and nitrogen are being measured by means of a mass spectrometer and a special pressure gauge.

(3) Reaction kinetics of titanium and zirconium with hydrogen, oxygen and nitrogen at very low pressures : Kinetic measurements of the metal-gas reactions in the pressure range from 10^{-5} to 10^{-6} Torr and in the temperature range of 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 : Molybdenum, titanium, iron and aluminum oxide and nitride films 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 with argon plasma are being investigated, and the formation mechanisms are studied.

(5) Chemical reactivity of iron nitride and silver oxide films prepared by sputtering: Chemical reactivity of the oxygen and nitrogen in the sputtered films with ethylene and hydrogen is being examined.

In addition, studies on the catalytic pump for hydrogen, the self-sustained electron emission from tin oxide films, and the adsorption of water by anodic oxide films on aluminum are also being made.

Oral Presentations

Quantatative Analysis of Minute Amount of Gases by a Quadrupole Mass Filter; M. Hashiba and T. Hanasaka: The Hokkaido Section Meeting of Japan Society of Applied Physics, Sapporo, Feb. 1973.

Behaviour of Residual Gases in the Hokkaido University LINAC during Operation (I); T. Hanasaka, A. Hasunuma, M. Hashiba and T. Yamashina: ibid.

Measurement of Pattern Coefficients of Various Gases in a Quadrupole Mass Filter —Sputter Ion Pump System (II); T. Hashiba, T. Hanasaka and T. Yamashina: The Spring Meeting of Japan Society of Applied Physics, Tokyo, Mar. 1973.

Improvement of Sensitivity in Omegatron Mass Spectrometer; T. Hanasaka: *ibid.*

Sorption of Hydrogen and Deuterium under Very Low Pressures and High Temperatures by Zirconium; M. Nagasaka T. Homma and T. Yamashina: *ibid.*

Effect of Ion Bombardment on Hydrogen Adsorption by Evaporated Nickel Films; K. Watanabe and T. Yamashina: ibid.

Preparation of Homogeneous Films of Copper-Nickel Alloys by means of RF Sputtering; T. Abe and T. Yamashina: The 28th Annual Meeting of the Japan Chemical Society, Apr. 1973.

Quantitative Measurement of Active Gases ranged in 10^{-2}–10^{-7} Torr by Sensitive Pirani Gauge; K. Watanabe, T. Hanasaka and T. Yamashina : *ibid.*

Reactivity of Chemisorbed Hydrogen on Evaporated Nickel Films ; K. Watanabe and T. Yamashina : *ibid.*

Reaction of Active Gases of Very Low Pressures with Zirconium and Titanium ; M. Nagasaka : The Regular Meeting of Japan Vacuum Society, Tokyo June 1973.

Effect of Imperfection of Crystal Surfaces on Chemical Reactivity of Solids ; T. Yamashina : The 4th Seminar on Thin Films and Surface Physics, Tokyo, June 1973.

Electronic State and Catalysis of Clean Surface of Cu–Ni Alloys ; Y. Takasu and T. Yamashina : The Meeting for Solid Surfaces at Tokyo University, Tokyo, July 1973.

Oxidation Process and Infrared Spectra of Evaporated Tin Films ; H. Fuse, S. Tanaka and T. Yamashina : The Hokkaido Section Meeting of Japan Chemical Society, Hakodate, July 1973.

Chemical Structure of Metallic Oxide Films Prepared by Reactive Sputtering Method ; T. Abe, T. Hanasaka and T. Yamashina, ibid.

Catalytic Activity and Alloy Composition of Clean Surfaces of Copper-Nickel ; T. Yamashina and Y. Takasu : The 2nd Japan-Soviet Catalysis Seminar, Tokyo Oct. 1973.

A Consideration on Catalytic Activity Factors of Clean Surface of Cu–Ni Alloys ; Y. Takasu and T. Yamashina : The Annual Meeting on Catalysis, Hiroshima, Oct. 1973.

IR Study on Silver Oxide Films Prepared by Reactive Sputtering ; S. Tanaka and T. Yamashina : *ibid.*

Sorption Kinetics of Hydrogen and Deuterium by Titanium at Elevated Temperatures ; M. Nagasaka and T. Yamashina : The 29th Annual Meeting of Japan Chemical Society, Hiroshima, Oct. 1973.

Behaviour of Residual Gases in the Hokkaido University LINAC during operation (II) ; T. Hanasaka, M. Hashiba and T. Yamashina : The 14th Annual Meeting of Vacuum Society of Japan, Tokyo, Nov. 1973.

Structure and Properties of Evaporated Tin Oxide Films (I) Oxidation Process of Films ; H. Fuse, S. Tanaka, T. Hanasaka and T. Yamashina : *ibid.*

Structure and Properties of Evaporated Tin Oxide Films (II) Self-Sustained Emission of Electrons from the Films ; T. Sa take, M. Hashiba, T. Hanasaka and T. Yamashina : ibid.

Preparation of Nitride Films of Molybdenum and Titanium by means of Reactive Sputtering ; T. Abe, T. Hanasaka and T. Yamashina : *ibid.*

PHSICAL METALLURGY LABORATORY

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

Students

T. Nakai, K. Konno, S. Ishiyama, M. Kobayashi,
T. Takahashi, H. Uetsuka, N. Yokoya, S. Kikuchi,
T. Nakaji and H. Matsuyama

This laboratory is investigating the aging phenomena of iron alloys, not only at a static state but also at a dynamical state under the condition of elevated temperature. Especially, the study of the interaction between the solute atoms and the point defects produced by the high voltage electron irradiation is the main activities. Also, the stress corrosion cracking of stainless steels is investigating. High speed straining electrode methode has been developed to examine the anodic dissolution and repassivation of emergent slip steps on the steel surface during deformation. Theoretical and experimental analysis has been made of the straining electrodes depends on the strain and also straining rate.

At the present time research is being carried out as follows:

(1) Effect of electron irradiation on aging phenomena of ferrous and Al base alloys. Point defects are produced by electron irradiation using an electron microscope of 650 kV accelerating voltage. After the irradiation, aging treatment is carried out in the microscope at various times and temperatures.

(2) Strengthening mechanism of ferrous alloys at elevated temperature. Fe–C alloys show the serrated flow due to a dynamical strain aging and the high work-hardening rate at the blue-brittleness temperature range. The relation between the mechanical property and the dislocation structure is being investigated.

(3) A relation between the dislocation motion and a Lüders band propagation. Some parameters, such as temperature depend-

ence of the propagation velocity, stress-velocity exponent of a dislocation motion and a stress concentration coefficient are analyzed.

(4) Dynamical behavior of the serrated flows in the work-hardening region. The velocity of deformation of Fe alloy during the serrated flow are being investigated.

(5) Beneficial effect of nickel in the stainless steel on the stress corrosion susceptibility in boiling magnesium chloride solution is analyzed by using the high speed straining electrode methode. The lower dissolution current on the fresh surface and also the slow repassivation rate is found for the higher nickel content alloys. Effect of minor elements, such as N, and Mo is also studied by the same methode.

(6) Hydrogen charging of pure iron is being studied. Blistering and intergranular cracking due to cathodic charging are found to be controlled by the heat treatment for annealing and aging. The higher density of blistering is observed at the carbide precipitation region, in which a small portion of cracks changes to transgranular path.

Oral Presentations

Deformation Strength at Elevated Temperature of α-Iron ; T. Takeyama : The First Section of Japan Inst. Metals, Feb. 1973.

Effect of the Electron Irradiation on Aging Phenomena of Fe–C Alloy ; H. Takahashi and T. Takeyama : The Spring Meeting of the Japan Institute of Metals, April, 1973.

Behavior of Point Defect in Steel ; T. Takeyama ; The 85th meeting of Iron and Steel Institute of Japan, April, 1973.

Fffect of Point Defect on Precipitation in Fe–C Alloy ; T. Takeyama and H. Takahashi : The Hokkaido Section Meeting of Japan Institute of Metals and Iron and Steel Institute of Japan, July, 1973.

Behavior of Carbon Atoms and Point Defects Produced by Electron Irradiation of Iron ; H. Takahashi and T. Takeyama : The Symposium of Japan Institute of Metals, Oct. 1973.

Effect of Point Defect on Precipitation in Fe–C Alloy (II) ; H. Takahashi and T. Takeyama : The Hokkaido Section Meeting of

Japan Institute of Metals and Iron and Steel Institute of Japan, Nov. 1973.

Enrichment of Chromium into the Passive Film of Stainless Steel. T. Shibata, G. Okamoto, K. Tachibana and K. Hoshino : The 8th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb. 1973.

Analysis of the Passive Film of Stainless Steel by Means of ESCA. G. Okamoto, K. Tachibana, K. Hoshino and T. Shibata : The Spring Meeting of the Japan Institute of Metals, April, 1973.

Behavior of Straining Stainless Steel Electrodes in the High Temperature 46% Maguesium Chloride Solution ; T. Shibata and T. Takeyama : The 20th Symposium on Corrosion and Protection, May, 1973.

Preparation Technigues of the Surface of Stainless Steel for the Electrochemical Measurement ; T. Shibata and T. Ishikawa : The Comittee of Preventing Corrosion in the Japan Society for the Promotion of Science, Jul., 1973.

Behavior of Straining Nickel Electrode in Sulphuric Acid Solution ; T. Shibata and T. Takeyama : The 40th Annual Meeting of the Japan Electrochemical Socsety, Aug. 1973.

Some Topics on the Strainihg Electrode ; T. Shibata : The Discussion Meeting on the Plastic Deformation and Anodic Dissolution Sponsored by the Japan Institute of Metals, Aug. 1973.

Behavior of Straining Fe–Cr–Ni Alloy Electrodes in Sulphuric Acid Solution ; T. Shibata and T. Takeyama : The Fall Meeting of the Japan Institute of Metals, Oct. 1973.

HIGH VOLTAGE ELECTRON MICROSCOPE LABORATORY

Prof. Dr. T. Takeyama, Mr. G. Tomita,
Mr. Y. Sato and Mr. S. Mochizuki

This laboratory was established April 1971, and has a 650 kV Hitachi High Voltage Electron Microscope, and a HSM-2 Scanning Electron Microscope.

This laboratory is open for research conducted by faculty members of this Hokkaido University and also tries to catalyze interdepartmental graduate education and research.

Effect of Sulfate and Chloride Ions on Corrosion Inhibition of Mild Steel by Chromate

S. Kawamura, N. Tanaka and M. Nagayama

Corrosion Engineering (Boshoku Gijutsu)
22, 500 (I973), No. 12.

Corrosion rates of mild steel in solutions containing chromate and sulfate or chloride ions were estimated at a pH of 8 by the polarization resistance method. The critial concentration of chromate above which corrosion rate is below 1 mdd increased with the increase of sulfate or chloride concentration. Presence of Ca^{2+} ions did not affect the value of the critical concentration. It was demonstrated for waters from different sources that rough estimation of the critial concentration could be made preliminarily as far as the concentrations of sulfate and chloride are known. (English)

Cathodic Polarizatios Characteristics of platinum in Chromic Acid Solutions and Mechanism of Electrodeposition of Chromium

Masakiyo Izumiya, Tetsupei Tamura
and Masaichi Nagayama

J. Chem. Soc. of Japan, Chemistry and Ind.
Chemistry (1973), 2275, No. 12.

Cathodic current-potential curves were measured for platinium in concentrated chromic acid solutions with and without addition of sulfuric acid. Each measurement was started with a clean platinium surface and the current was recorded at a certain period of time after applying a constant cathode potential. The current-potential curves obtained for the solution containing sulfate ion were characterized by the existence of four current waves of I, II, III and IV appearing respectively around +0.5, −0.3, −0.8 and −1.0 V (vs. SCE). The wave II was absent for the soultion free from sulfate ion. The partial currents for electrode reactions as well as the amount and the composition of surface deposits were determined as a function of the cathode potential, by means of chemical analyses. For the solutions containing sulfuric acid, reactions corresponding to the waves of II, III and IV were found to be (Cr (VI)→Cr $(III)_{aq}$, *$H^+ \rightarrow H_2$), (Cr (VI)→Cr $(III)_{aq}$, $H^+ \rightarrow H_2$, *Cr (VI)→Cr (O)) and (Cr (VI)→Cr $(III)_{aq}$ $H^+ \rightarrow H_2$, Cr (VI)→Cr (O)), respectively. Reactions marked with asterisks were observed in the descending part of the waves. Formation of Cr $(III)_{aq}$ was not observed at any waves for the solution free from sulfate ion. The surface of the specimen was covered with a thin layer of hydrous chromic oxides containing chromate and sulfate ions, the thickness of which being increased with lowering potential and decreasing sulfate concentration. The black chromium films formed in the solution free from sulfate ion were composed of hydrous chromic

oxides, metallic chromium and crystalline chromic oxide. The polarization characteristics and the mechanism of deposition of chromium were discussed in detail based upon these findings. (Japanese)

Factors Limiting the Sensivity in Cotrolled Potential Coulometry

H. Ohashi

Analytical Instruments **11**, 184 (1973), No. 3.

The controlled potential coulometry has been applied for the corrosion studies as well as usual purposes of chemical analysis. A newly designed device, which has been developed by the author, has been firstly applied to measurments of the corrosion rates of iron and other metals under the pH-static conditions. This device is also applied for other varieties of physico-chemical measurements in aqueous solutions. Factors limiting the sensitivity in the controlled potential coulometry were reviewd on the general viewpoints including problems in our method. The sensitivity was mainly limited by two origins ; one is electronic and the other electrochemical. The former is correlated with the order of magnitude of composite noise and drift in the potentiostat circuit. It is directly related with the lowering of the signal-noise ratio of whole measuring system. Remarkable improvements of noise and drift were made by utilizing the extremely stabilized electronic potentiostat which was constructed of an A. C. differential amplifier and an output device for electrolytic current. Proper control of potentiostat circuit conditions was also essential to keep the noise and the drift at the lowest level. The most significant electrochemical factor is the elevation of the conversion ratio of the electrolytic current signal against the concentration signal. This can be attained simply by the design of electrolytic cells with a large ratio of the effective surface area of electrode to the volume of electrolytic solution. The proper conditioning of electrodes for repeated uses, the precise temperature control within ±0.03°C, and the electromagnetic shield around the electrolytic cell were all effective in any cases. Under the best conditions, the electrode

potential could be kept constant within the small range of fluctuation less than ±10 μV, which corresponds to the pH change less than ±0.00015. (Japanese)

ABSTRACTS

An Electrochemical Aspect on Pressure Precipitation of Nickel

T. Nagai and M. Sato

International Symposium on Hydrometallurgy,
Chapter 2, Eds. D. J. I. Evans and R. S.
Shoemaker, AIME, New York (1973)

Electrochemical measurements have been carried out in an autoclave to investigate the electrochemistry of hydrogen precipitation of nickel from acetate buffered solution. After having previously obtained the rate equation for this reaction we have now made a concentrated effort to explain the rate equation electrochemically. A saturated NaCl-type Ag/AgCl reference electrode has been improved so that it can be used in an autoclave. Polarization curves for the reaction, $H_2 \rightleftharpoons 2\,H^+ + 2\,e$, on nickel electrode were measured in sulutions free from nickel ions at 185°C, and the paralel curves were obtained by changing P_{H_2} and pH for forward and reverse reactions, respectively. Polarization curves in nickel solutions were complex, probably because the potential of hydrogen electrode is close to that of nickel and the nickel surface altered during polarization. Then, the nickel electrode potential and the reaction rate were measured simultaneously during pressure reduction at various hydrogen pressures and at various nickel concentrations. The reaction rates in terms of current density were plotted to obtain the local polarization curves for reactions $Ni^{2+} + 2e \rightarrow Ni$ and $H_2 \rightarrow 2\,H^+ + 2e$. The anodic and catnodic local polarization curves exhibit a potential dependency. Therefore it is likely that the pressure reduction can be regarded as a coupled electrode reaction. (English)

The Structure and Reactivity of Nickel Hydroxide.

M. Sakashita and N. Sato

Bulletin of the Chemical Society of Japan,
46, 1983 (1973), No. 7.

This paper examines the correlation between the structure and the reactivity of nickel hydroxide, using X–ray diffraction, DTA, IR spectroscopy, and gravimetry during dehydration. The degree of crystallization of β-nickel hydroxide depends on the preparation conditions of the hydroxide. Highly-crystallized β-nickel hydroxide has "free" hpdroxyl groups, as is to be expected from its brucite structure. Poorly-crystallized β-hydroxide, however, has "hydrogen-bonded" hydroxyl groups ; this finding disagrees with a previous result that "hydrogen-bonded" hydroxyl groups were found to exist only in α-form nickel hydroxide. The dehydration of the hydroxide is shown to take place in a first-order kinetics with the activation energy which increases as the crystallization extends. (English)

Formation and Dissolution of Porous Anodic Oxide Films on Aluminum

M. Nagayama and H. Takahashi

Bulletin of Japan Institute of Metals,
12, 449 (1973), No. 7.

Investigations conducted recently in authors laboratory on anodizing of aluminum were described. This review paper consists of the following topics: (1) Formation and dissolution of oxide at the initial stage of anodizing. Change of current with time under a constant anodizing potential was explained in terms of the changes of geometrical structure and dissolution behavior of the film. The formation of the vacancies of Al^{3+} ions at the top of the barrier layer and the penetration of H^+ ions to these positions were suggested. (2) Distribution of electrolyte anions in the film. Distribution of phosphate ions across the pore-wall of the film formed in phosphoric acid solution was measured by means of a fractional dissolution of the film in sulfuric acid solution. It was shown that phosphate ion concentration gradually increases with the distance inwards from the surface of the pore-wall but decreases steeply to almost zero near the center of the pore-wall. Mechanism explaining the occurance of such a distribution is described. (3) Current recovery phenomena. It is known that, when the anodizing voltage is suddenly lowered, the current immediately drops to almost zero but commences to increase gradually after a certain period of time and reaches a steady value. The structural changes of the film associated with the phenomena is described based upon the electronmicrographs obtained by the aid of ultra-thin sectioning of the film. The mechanism of the phenomena is discussed in detail. (Japanese)

Electron-microscopy of Porous Anodic Oxide Films on Aluminium by Ultra-thin Sectioning Technique Part. 1

The Structural Change of the Film during the Current Recovery Period.

H. Takahashi, M. Nagayama,
H. Akahori and A. Kitahara

J. Electronmicroscopy, **22**, 149 (1973), No. 2.

The structural change of the porous anodic oxide film on Al was traced by electronmicroscopy during the current recovery period appearing after an abrupt lowering of anodizing voltage. An ultra-thin sectioning of the film was found to be quite useful. Based upon the findings, the mechanism for explaining the current recovery phenomenon was discussed in detail. (English)

Ellipsometric Study of Anodic Passivation Films on Metals.

N. Sato and K. Kudo

Annual Report of the Asahi Glass Foundation
for the Contribution to Industrial Technoloqy,
(AGKGAA), **21**, 1 (1972).

Ellipsometric study combined with electrochemical measurements has been made of the anodic passivation films on iron, nickel and iron-nickel alloys in a neutral sodium borate-boric acid solution. In the case of iron, the film is composed of a hydrous ferric oxide, probably γ-Fe_2O_3, of which the average optical constant is 2.55–0.35i, and the thickness increases linearly with rise of potential from 9 to 50 Å in the passive potential region. The film formed on nickel has the optical constant of 2.7-0.25 i, which is assumed to be NiO, and its thickness is in the range 4 to 13 Å increasing with the potential. Nickel dissolves at relatively small rates in the whole range of passivity, but exhibits a secondary passivation in a potential range where oxygen evolution begins to occur. No nickel dissolution is observed in the secondary passivity region where a phase oxide film is formed. It is found that the thickness of passivation films formed on iron-nickel alloys is not in a linear relation with the nickel content of alloy substrates. (Japanese)

Anodic Passivation Films on Iron in Acidic and Basic Solutions.

T. Noda, K. Kudo, and N. Sato

Journal of the Japan Institute of Metals,
37, 1088 (1973), No. 12.

The anodic passivation films formed on iron in sodium phosphate, borate and hydroxide solution at various pH values have been investigated by means of ellipsometry, thermogravimetry, and electrochemical analysis. Ellipsometric measurements reveal that the film consists of an inner layer of γ-Fe_2O_3 and an outer layer of hydrous ferric oxide. The thickness of the inner layer increases linearly with rising polarization potential, and the potential at which the inner layer vanishes is found to agree well with the equilibrium potential of γ-Fe_2O_3 formation on iron in the pH range from 1 to 12. The outer layer appears to depend on the pH and anion of the solution but its thickness is almost independent of the potential at which the film is formed. These results indicate that the polarization of film formation occurs in the inner layer irrespective of the solution pH. At constant over-potential, therefore, the inner layer thickness is constant independent of the solution pH in neutral and basic solutions where no dissolution of the film occurs. In acidic solutions, however, the inner layer becomes thin as the solution acidity increases because of increase of the rate of film dissolution. The outer layer thickness decreases with decreasing solution pH in the basic and neutral pH range and is negligibly small in acidic solution. It is also shown that the more basic solution results in the more amount of water diffusing into the outer layer. A film model is proposed in which the outer layer is affected by the solution pH, while the inner layer is determined only by the over-potential of film formation. (Japanese)

Ellipsometric Study of the Passivation Film on Iron in Neutral Solution.

T. Noda, K. Kudo, and N. Sato

Journal of the Japan Institute of Metals,
37, 951 (1973), No. 9.

The anodic passivation film formed on iron in neutral borate-buffer solution has been studied by using ellipsometric, electrochemical, and gravimetrical techniques. The film can be dissolved from its outer surface by applying a cathodic current in borate-buffer solution at pH 6. 35 in which the reductive dissolution,

$$Fe_2O_3 \cdot nH_2O + 6H^+ + 2e \longrightarrow 2Fe^{2+} + (n+3)\ H_2O,$$

proceeds at 100 per cent current efficiency. Ellipsometric measurements carried out during the galvanostatic-cathodic reduction of the film in this solution reveals that the film consists of two layers, an inner layer with the optical constant 3.0–0.5i and an outer layer with the constant 1.8–0.1i. It is also shown that the density of the inner layer is in agreement with that of γ–Fe_2O_3. The inner layer thickness increases linearly with the anode potential, and the potential extrapolated at zero thickness of the inner layer corresponds to the equilibrium potential of the anodic formation of γ–Fe_2O_3,

$$2\,Fe + 3\,H_2O \longrightarrow \gamma\text{–}Fe_2O_3 + 6\,H^+ + 6\,e.$$

The outer layer, however, is not directly related to the anode potential. Thermo-gravimetrical measurements indicate that the film contains some amount of water, which is concentrated in the outer layer. The average composition of the outer layer is estimated as $Fe(OH)_3$. A film model is proposed in which the inner layer of anhydrous γ–Fe_2O_3 is the cause of the potential drop in the film producing a field intensity of 5.6×10^6 V/cm and the outer layer of hydrous ferric oxide depends on the solution environment and passivation process. (Japanese)

Anodic Oxide on Silver in Alkaline Solution.

N. Sato and Y. Shimizu

Electrochimica Acta, **18**, 567 (1973), No. 8.

The anodic oxide films formed on silver in 0.1 N KOH solution have been chemically analyzed for the valency of silver ion. The anodic oxide formation proceeds in two stages, which are distinguishable not only in galvanostatic and potentiodynamic oxidation curves but also in the potential-current and the potential-charge curves obtained by potentiostatic oxidation. The average valency of Ag ion in the oxide formed in the first stage is estimated to be Ag^+ and the one in the oxide formed in the second stage is Ag^{2+}. The galvanostatic reduction of AgO formed in the second stage of oxidation occurs via two potential arrests. At the first arrest of potential the reduction of Ag^{2+} to Ag proceeds but is not completed. The transition from the first to the second potential arrest, therefore, does not correspond to the complete reduction of AgO to Ag_2O. (English)

Sorption Kinetics of Oxygen at Very Low Pressures by Zirconium

M. Nagasaka, F. Uyeda and T. Yamashina

Vacuum **23**, 51 (1973), No. 2.

The sorption rate of oxygen by zirconium at very low pressures of 4×10^{-6} to 4×10^{-4} Torr has been investigated in the temperature range 500–850°C using a microbalance. The rate law of sorption was separable into two types, i. e., the linear rate law in the initial period and the parabolic rate law in the latter period. In the initial linear sorption, the rate was exactly proportional to the oxygen pressure at each temperature. The date of sorption kinetics of zirconium were rearranged from the viewpoint of vacuum technology, i. e., sticking probability and pumping speed in bulk gettering. The transition in the rate law of sorption is discussed on the bases of Wagner's model which involves simultaneous scale formation and oxygen dissolution into the metal bulk. (English)

On The High Temperature Syntheses of FeS-Based Sulfides in Fe–Cr–S and Fe–Cu–S Systems

K. Nishida and T. Narita

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 67, 127 (1973), July.

In order to obtain basic data required for the study of sulfidation of metals and alloys, sulfides in an Fe–Cr–S system as well as an Fe–Cu–S system were synthesized under various conditions and their lattice parameters as well as their solid solubilities were determined. The results obtained show that in the Fe–Cr–S system a spinel type crystal such as $FeCr_2S_4$ was formed under $P(S_2)=1$ and 10^{-3} atm. Other numerous types of Cr-sulfides were produced under various temperatures and in different compositions, while, in the FeS–CrS system no spinel crystal was formed, but two-phase mixtures of FeS and CrS were noted. The solid solubility of CuS is found to be greater than that of Cu_2S in the Fe-monosulfide. In consideration of the dissolution states and their mechanisms of these sulfides into FeS it was suggested that the solid solubilities and dissolved states have an intimate connection with the ionic state and the lattice defect formation in FeS crystals. (Japanese)

On the Sulfur Distribution in FeS Scale Formed on Pure Iron at 700°C

T. Narita and K. Nishida

Transactions of The Japan Institute of Metals
14. No. 6, 447 (1973), November.

The sulfur distributions in the iron sulfide scale formed at 700°C under various sulfur pressures were determined by X-ray diffraction. The gradient of the sulfur distribution in the scale is not linear, different from the results in the literature. A very sharp decrease in sulfur content and some flat range of composition of about 51.5 at %S are observed near the Fe/FeS interface and at the inner part of the scale, respectively. The inter- and self-diffusivities of iron were calculated according to Fick's second law and Darken's relation as functions of distance and composition, based on the sulfur distributions and were an order of 10^{-6} and 10^{-8} cm^2/sec, respectively. The self-diffusivity of iron was also calculated by use of several other methods and their results were compared with each other. The extraordinary high diffusivities were obtained at the composition of about 51.5 at %S which corresponded well to the composition of the maximum value of a_0 parameter of FeS. This behavior may be attributed to the generation of the stress by deformation of the scale, the variation of the a_0 parameter with sulfur content in the scale, and also the annealing effect on the stress during corrosion. The effect of the inner scale on the sulfur distributions in the outer scale was also examined and showed to result in the higher sulfur content in the outer scale. The SEM observations of the inner scale fractured mechanically revealed the formation of voids in it, suggesting contours of the perforating dissociation of the outer scale crystal. (English)

The Effect of Sulfur Pressure on the Iron Sulfide Scale Growth at Elevated Temperature

T. Narita and K. Nishida

Transactions of The Japan Institute of Metals
14. No. 6 439 (1973), November.

In order to elucidate the sulfidation behavior of pure iron at high temperature, kinetic studies were carried out as functions of sulfur pressure and temperature, and the sulfide phases of the scale formed were examined. The sulfidation obeys a parabolic rate law, but the slopes of the log-log plots of sulfur pressures and corrosion rate constants change in the range 1/3.5 to 1/5.7 depending on the sulfur pressure. The phases and preferred growth orientations of the scale were identified by the X-ray diffraction method. The results showed that the scale was composed of the pyrrhotite, troilite, and Fe_7S_8 phases, and that at higher pressures the $(00\,l)$ planes were normal to the scale growth direction, while at lower pressures the (110) and/or $(10\,l)$ planes were normal to that direction. The SEM observation of the scale formed at 800°C revealed that the hexagonal step-like feature of the surface changed into a more flattened one with decreasing sulfur pressure. From the growth mechanism of the scale it was evident that these sulfidation behavior was closely related to the vacancy configulation and diffusivity of iron ions in the scale and also to the adsorption of sulfur atoms on the particular sites of the scale surface. (English)

On the High-Temperature Corrosion of Fe-Cr Alloys in Sulfur Vapor

T. Narita and K. Nishida

Oxidation of Metals, **6**, 157 (1973), No. 3.

The mechanism of sulfidation of Fe-Cr alloys ranging from 8 to 97 wt.% chromium was determined from studies of scale structures, surface morphologies of scale, and reaction kinetics. Although the kinetics of sulfidation were quite similar to those previously determined by Mrowec et al., the structures in the present work were different, being triplex in nature. The growth mechanism of each layer was determined, and the overall sulfidation behavior was compared to the oxidation behavior. Many similarities between the two corrosion processes were observed. (English)

High-Temperature Crrosion of Low Cr-Fe Alloys in Sulfur Vapor

T. Narita and K. Nishida

Oxidation of Metals, **6**, 181, (1973), No. 3.

The sulfidation behavior of low Cr-Fe alloys was studied over the range of 700–900°C under 1 atm of pure sulfur vapor. Sulfidation of alloys with 3.7 and 7.4 wt.% Cr does not follow the parabolic rate law at 750–800°C, although for other alloy compositions and temperatures it obeys that law. Sulfide scales consisted of a three-layer structure. The outer layer was FeS, but the inner and intermediate layers contained FeS, $FeCr_2S_4$, and Cr_3S_4, their relative amounts and morphologies depending on the corrosion temperature and alloy composition. Increasing Cr contents resulted in a change in the morphology of $FeCr_2S_4$ from dispersed particles to a thick layer. Ultimately, $FeCr_2S_4$ was displaced by Cr_3S_4. The formation of $FeCr_2S_4$ and the scale growth mechanism are discussed also. (English)

On the Kinetic and Thermodynamic Studies on the Cr–S System at High Temperature

Corrosion Science, **13**, 759. (1973).

K. Nishida, K. Nakayama and T. Narita

In order to elucidate the sulphidation behaviour of chromium at high temperatures, kinetic and thermodynamic investigations were carried out. Firstly, the P–T diagram of Cr_2S_3 (r.h.), Cr_2S_3 (tr), and Cr_3S_4 phases was determined. Then, kinetic studies and structural examination of the scales were performed. The sulphidation obeys a parabolic rate law, but Arrhenius plots of the rate constants show no straight lines. Scales were composed of many Cr sulphides and their distributions in the scales changed depending upon the corrosion conditions. A similar variation was observed in the surface morphologies. The mechanism of scale growth is discussed based on kinetic factors and lattice defects. (English)

Some Observations on the Interdiffusion between Fe and Fe–Al Alloys

K. Nishida and T. Narita

Transactions of the Japan Institute of Metals,
14, 431 (1973), No. 6.

Experiments were carried out to clarify the fundamental multiphase-diffusion behaviors in Fe–Al alloys. At first, the etched structure and the hardness for each intermetallic compound in the alloys were examined in the normal state. For further observations, the diffusion couples prepared by the plating of Fe on the alloys were annealing at 800°C for several hours, and the diffusion couple with the alloy containing the Al phase was annealed at 610°C for 10 hr. The experimental results revealed that the ζ phase ($FeAl_2$) had a smooth boundary with the α phase, and the η phase (Fe_2Al_5) transformed in the sequence of $\eta \to \zeta \to \alpha$. During the transformation of the η phase, however, a considerable amount of the ζ phase was observed between the η and α phases and the irregurality in the $\zeta - \eta$ boundary which was dependent upon the orientation of the original η phase was observed. With increase in Al content, in the η phase, a new η phase which protruded locally into the Fe layer appeared and consequently the ζ phase was considerably reduced. The higher Al content alloy of the $\eta_{max}+\theta$ phases or the θ+Al phase showed a local growth of the η phase, resulting in formation of the so-called bridges, the detachment of the plated Fe layer from the alloy substrate, and the formation of many voids in the newly formed η matrix. In order to explain the above phenomena, the change in volume with the phase transformation and the effect of the anisotropy of the η phase were taken into account. Some calulations using the properties of the intermetallic compounds showed that above behavior would be ascribed to the high-diffusivity of Al atom released from the θ phase by the $\theta \to \eta$ reaction or from the Al phase, and also to the creation of the new η phase at the Fe-Alloy interface. (English)

Bilayered Oxide Scales Formed on Nickel

T. Ueno

Transactions of the Japan Institute of Metals,
14, 267, (1973), No. 4, July.

Bilayered scale of NiO is formed on not only impure but high-purity nickel by heating in air at temperatures of 900 to 1,200°C for times up to 72 hr. It is found that scales consist of two layers which are metallographically and/or crystallographically different from each other. They can be classified into several types accoridng to their metallographic and crystallographic structures. (English)

Discontinuous Lüders Band Propagation of α-Iron in the Blue-brittleness Temperature Range

H. Takahashi and T. Takeyama

J. Japan Inst. Metals, **37** (1973), 441.

The present work was concerned with an experimental study of Lüders band propagations in the blue-brittleness range and its analysis of some parameters, that is, dislocation structures, stress dependence of the propagation velocity, and others. The specimen used was an α-iron containing 0.006 wt% carbon. The correlation between the stress drop and the decay time during the band propagation was obtained by using an oscillographic recorder. Also, dislocation structures were observed by means of transmission electron microscopy. Dislocation structures were tangled and the average dislocation density was about $8\times10^9/\text{cm}^2$ in the temperature range from 160 to 250°C. The magnitude of the stress drop did not directly depend on the amount of dislocation generated and its multiplication rate, but on the width of Lüders band propagated. The propagation velocity of Lüders band could be expressed by the same relation as the stress dependence of dislocation velocity. The dislocation velocity exponent, m, derived from the relation between the stress drop and the decay time was approximately 18 in the temperature range investigated. With increasing temperature, initial velocities of Lüders propagation became higher, i. e. about 55.6 cm/sec at 160°C, 312.4 cm/sec at 200°C, and 595.5 cm/sec at 250°C. This temperature dependence of the velocity could be associated with that of the stress concentration factor caused by dynamical strain ageing near the Lüders band front. (Japanese)

The Effect of Electron Irradiation on Quench-Aging of Fe–C Alloy

T. Takeyama and H. Takahashi

J. Phys. Soc. Japan, **35** (1973), 939.

Vacancies and interstitials were produced in a solution-quenched Fe–0.025 wt% C alloy by using electrons ejected from a high voltage electron microscope, and the effect of excess point defects on the aging behavior was studied. The specimens were irradiated for 20 min at room temperature by 650 kV electrons and heat-treated. The specimens aged below 240°C showed no visible precipitates in the irradiated area. As a large number of vacancies must remain in the irradiated area, it appears that supersaturated carbon atoms migrate to individual vacancies and are trapped by them to form C–V pairs, then resulting in the suppression of the carbide precipitaion. The dissociation of the C–V pair and precipitation of the cementites in the irradiated area were observed at the temperature above 240°C. The C–V pair is highly stable even at the precipitation temperature of the cementite because of the high binding energy between carbon atoms and vacancies. An unusual growth of cementite particles was observed in the irradiated area after aging above 250°C. In this case, carbon atoms leaving from the traps may be absorbed to the cementite-matrix interface in order to release the coherency strain developed during the growth of precipitate, thus accelerating the growth of the cementite. (English)

CRGHU

Strength and Dislocation Structures of α-Irons Deformed in the Blue-brittleness Temperature Range

T. Takeyama and H. Takahashi

Trans. Iron and Steel Inst. Japan, **13** (1973), 293.

The relationship between the dislocation structure and the tensile property has been investigated in the temperature range from the room temperature to 400°C in four kinds of α-iron with different carbon contents. The grain size dependence of both yield and flow stresses has also been studied in the same temperature range. The serration phenomenon is observed in the stress-strain curve in a specific temperature range for each specimen, where both a high flow stress and a high work-hardening rate are shown. The temperature at which the serration occurs shifts to the higher temperature side with a decrease in the carbon content. The higher the solute carbon content is, the greater both the flow stress and the work-hardening rate become. The flow stress for each specimen is analyzed as a function of the Petch parameters (k and σ). Petch parameter for flow stress, k_f is identical with for yield stress, k_y in the blue-brittleness range, but the frictional stress σ_i seems to increase with elevating the deformation temperature. This high value for frictional stress corresponds well to the high work-hardening rate. The change in flow stress component at each deformation temperature is strongly related to that in σ_i value. In the temperature range in which serrations are observed, deformed specimens show the high dislocation density and very small cell structures. These rapid increases in both the flow stress and the work-hardening rate are, therefore, related directly to the high rate of dislcoation multiplication. (English)

SEM Observation on Brittle Fracture Surface of Steel

I. Takahashi, T. Saito, T. Noguchi
and K. Nagaoka

Bulletin of The Faculty of Engineering,
Hokkaido University, 67 (1973), June.

The features of brittle fracture were investigated by means of scanning electron fractography. Notched tensile specimens of mild steel with ferritic-pearlitic structure were fractured at liquid nitrogen temperature. The grain size of the specimens were 100 μ and 200 μ. The entire fracture surface (5×5 mm) was observed and covered by pictures with SEM. Tracing of river patterns of ferrite and pearlite facets clearly reveals the origin and the route of propagation in brittle fracture. Brittle cracks seem to commence within the ferrite grains or at the boundary of the ferrite-pearlite grain at a depth of a few grains below the notch root. With a notch radii of 1 mm, the origin was at a depth of 0.3 and 0.5 mm below the notch root, and with notch radii of 0.25 mm, the origin was at a depth of 0.15 and 0.2 mm below. Brittle cracks propagating to the entire fracture surface along many different routes, breadthwise and depthwise were traced. Macroscopic "tear lines" were at times formed between two different routes. (Japanese)

On the Rupture Strength of Notched Cast Iron

T. Noguchi and K. Nagaoka

IMONO, 45, 1. (1973), Jan.

Some experiments were carried on the rupture tensile strength of cast iron with cylindrical notches. Notch strength of cast iron varied according to the grade of strength and sharpness of notch. In FC 30 and FCD 45, it was recognized that the rupture strength for a certain region of α (form factor) was higher than the tensile strength obtained by unnotched specimen. Such increase of strength with notched metal is explained by the plastic constraint effect of tri-axial stress state under the notch. In the region of large α (sharp notch region) the notch strength tended to become almost constant in each cast iron. The notch sensitivity ratio in this region was 1.2, 0.95 and 0.85, respectively. This behavior is thought to be due to the micro notch of graphite flakes which may affect the sharp notch root. According to the characteristics on the notch strength showed in the experiment, it was suggested that the notched cast iron should be treated as a ductile metal with an outer macro notch and inner micro notches. Namely, cast iron is essentially ductile, but becomes brittle with micro defects in it. Cast iron FCD 45, FC 30 and FC 20 are ductile in this order. (Japanese)

On the Tensile Rupture Strength of Notched Cast Iron

T. Noguchi

Journal of The Society of Material Science,
Japan, 22, 235 (1973), Apr.

Using plate tensile specimens with notches of various sharpness, the notch strength of FC 25 class cast iron was examined. To analyse the stress distribution for blunt notch, the finite element method was applied. The rupture strength of cast iron decreased by the notch in plate specimen with increasing the sharpness of notch. Thus, the criterion that the average stress of notch section is constant was not valid. But in the region of sharp notch ($\rho < 0.5$ mm) the notch strength of cast iron became almost constant. The stress analysis by the finite element method showed that the specimen with a blunt notch ($\rho = 10$, 15 mm) ruptured when the maximum stress under the notch reached the tensile strength of this iron. Thus, the maximum stress criterion was valid. Though the rupture condition for the sharper notch was not analysed numerically, it was suggested that the rupture strength was influenced by the stress gradient besides the maximum stress. The tendency of saturation of strength in the region of sharp notch is thought to be due to the microscopic notch effect of graphite flakes. (Japanese)

On the Growth of Flake Cast Iron in Vacuum

M. Sōma and K. Nagaoka

IMONO, 45, 5 (1973), May

A flake cast iron of FC 25 class was heated repeatedly to 950°C in high vacuum up to the final stage of the growth. The iron grew continuously to the maximum of 19.4% after 235 heats, and in the final stage a slight contraction occurred. The growth process of this iron up to the final stage was divided into four stages. In the first stage the growth rate decreased rapidly; in the second stage the iron grew at a constant rate; and in the third stage the growth was saturated. As the iron grew, the strcuture became porous and graphite was redistributed in the matrix and around graphite flakes. With a scanning electron microscope these structural changes were observed in three dimensions. Over about 5% of linear growth the inner cavities were contacted and opened through the matrix to the surface, and the structure of iron was changed to be sensitive to oxidizing and other influences of heating atmosphere. The average coefficient of thermal expansion in the austenite region decreased during heatings from 43×10^{-6} at the initial stage to 28×10^{-6} at the final stage. This thermal change seemes to correspond to the decrease of the migration rate of graphite in the cast iron. (Japanese)

Anodic Behavior of Copper in Molten Alkali Nitrates

T. Notoya

J. Electrochem. Soc. Japan (DENKI KAGAKU)
41, 779 (1973), No. 10.

The electrochemical behavior of copper at anodic potentials in molten $NaNO_3$ and KNO_3 at 300°C has been investigated. The passivation of copper induced by anodic polarization indicates a characteristic peak current at 0.08 V against the Ag/Ag^+ reference electrode. Copper oxides formed on the electrode above the potential corresponding to the peak current were determined by X-ray analysis to be Cu_2O and CuO, while only Cu_2O was formed at spontaneous potential. At the potential above 0.20 V remarkable anodic dissolution of the passive copper was observed. A possible mechanism of the passivation and the dissolution of copper in the melt is discussed. (English)

Anodic Polarization Behavior of Metals in Molten $NaNO_3$-KNO_3 Eutectic at 300°C

T. Notoya and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
41, 865 (1973), No. 11.

Anodic polarization characteristics of 14 kinds of metals were obtained by a potential sweep method in an eutectic mixture of $NaNO_3$ and KNO_3 at 300°C. The corrosion potentials of the metals were measured before and after polarization against a silver reference electrode. The anodic polarization characteristics can be divided into four groups from the shape of the curve. (1) An abrupt increase of anodic current with potential was observed for Pb, Cd, Ag, Zn, and Ni. (2) A steep rise of the anodic current from the potential about 0.80 V was observed for Pd, Fe, Pt, and stainless steel. (3) Passivation was observed for Cu and W. (4) At more positive potentials than 1.0 V anodic current increased, but the current was comparatively small, because of a semiconductive oxide film formation for Ti, Ta, and Al. (English)

Electrochemical Studies on the Dissolution and Deposition of Aluminum in Molten Aluminum Chloride-Alkali Chloride Systems (Part 1)

Equilibrium Potential of Chlorine Electrode and Aluminum Electrode in Molten $AlCl_3$–NaCl Mixtures

T. Sato, T. Ishikawa, and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
41, 123 (1973), No. 2.

The chlorine electrode potential vs. an Ag/AgCl (0.08)–NaCl (0.40)–$AlCl_3$ (0.52) reference electrode was measured in molten aluminum chloride-sodium chloride mixtures at 200°C, and was found to depend considerably on the composition of the mixtures, and indeed within the composition range of aluminum chloride of 50.0–64.7 mol% ; the activity of chloride ions may change by the order of 10^5. The values of aluminum electrode potential calculated from the activity of chloride ions obtained in the present study exactly coincide with the measured values. From these results, the equation $Al + 4\,Cl^- \rightleftharpoons AlCl_4^- + 3\,e$ was assumed to describe a reasonable electrode reaction in deciding the equilibrium aluminum electrode potential. (Japanese)

Electrochemical Studies on the Dissolution and Deposition of Aluminum in Molten Aluminum Chloride-Alkali Chloride Systems (Part 2)

Solubility of Silver Chloride and Behavior of a Silver Reference Electrode in a Molten Aluminum Chloride-Sodium Chloride System

T. Sato, H. Yasunaka, T. Ishikawa,
and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
41, 713 (1973), No. 9.

In order to develop the electrode system Ag/AgCl–NaCl–$AlCl_3$ used for the reference electrode in molten aluminum chloride-alkali chloride systems, the solubility of silver chloride in these melts and the dependence of the potential of this electrode on composition, temperature and time were examined. From the solubility data, it is presumed that the behavior of silver chloride in the melts is similar to that of sodium chloride, because the relationship $N_{AgCl}+N_{NaCl}\fallingdotseq N_{AlCl_3}$ is to hold when the melt is saturated with silver chloride. At a constant ratio of AgCl/NaCl, the greater the concentration of aluminum chloride, the more noble the potential of this electrode becomes. At constant concentration of aluminum chloride, the relationship between electrode potential and the logarithm of the concentration of silver ion is linear at temperatures from 160° to 300°C. At constant compositions of the melt, electrode potential increased gradually, reaching a constant value after about two hours. Contrary to expectation, this electrode showed higher potential than a silver electrode in the pure silver chloride melt. (Japanese)

Electrochemical Studies on the Dissolution and Deposition of Aluminum in Molten Aluminum Chloride-Alkali Chloride Systems (Part 3)

Studies on the Electrochemical Deposition and Dissolution of Aluminum and the Codeposition of Alkali Metals with Aluminum in Molten Aluminum Chloride-Alkali Chloride Mixtures

T. Sato, T. Ishikawa, and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
41, 446 (1973), No. 6.

The electrochemical deposition and dissolution of aluminum electrodes in molten aluminum chloride-alkali chloride mixtures have been investigated using rotating cylindrical electrodes. The limiting current density of the deposition process has been found to be approximately proportional to the 1/2th power of rotational velocity of the electrode. Under steady state conditions, concentration overpotential seems to predominate among all overpotentials measured. An apparent activation energy of 5–7 kcal/mol. was found on the basis of the temperature dependence of the current density at various potentials. On the basis of the composition dependence of the cathodic limiting current density, the rate-determining step of aluminum deposition under steady state appears to be a diffusion process with such complex ions as $Al_2Cl_7^-$ in the melt. The anodic dissolution of aluminum in the melt was thought to be controlled by a diffusion process of some anodic products from the anode surface. Codeposition of alkali metals with aluminum was found at certain potentials which were far nobler than that predicted from the equilibrium decomposition voltage of alkali chlorides. (Japanese)

Relation Between Catalytic Activity Pattern anb Surface Composition of Cu-Ni Alloy -An Application of Auger Electron Spectroscopy to the Study on Catalysis-

Y. Takasu and H. Shimizu

J. Catalysis **29**, 479 (1973), No. 3.

Changes in surface composition of copper-nickel alloy plates with various pre-treatments were studied by means of Auger electron spectroscopy. The surface composition was found to be considerably changed from the bulk of alloy samples by the pre-treatments, namely the surfaces of the nickel-rich alloys are enriched with copper, while those of the copper-rich alloys are with nickel. Comparing the relations between the catalytic activity patterns of copper-nickel alloys and the pre-treatments of them which have been published by many authors, the original activity pattern of the catalyst is estimated. (English)

Catalytic Activity and Alloy Composition of Clean Surfaces of Copper-Nickcl

T. Yamashina and Y. Takasu

The 2nd Japan-Soviet Catalysis Seminar on New
Approach to Catalysis, Preprint p280 (1973).

The relation between catalytic activity in 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 alloys increase. The catalytic activity K_m could be expressed by an equation,

$$\log K_m = aX + b\,,$$

where X is content of nickel in alloys and a and b are constants, while work function Φ of copper-nickel alloys showed to change linearly with the alloy composition, i. e., $\Phi = cX + d$ (c and d: constants).

The catalytic activity factors of copper-nickel alloys could be discussed from the view point of surface electronic state, by applying the coherent potential approximation. (English)

Comparative Studies of Electrochemical Desalination: Ionic Membrane Electrodialysis Desalination,

N. Sato and K. Kudo

Report on "The Study of Developing Effective
Utilization of Natural Water Resourses"
sponsored by the Ministry of Education
of Japan, p. 39 (1973).

The ion membrane electrodialysis process which has been developed in the latter half of this centry has made its technical advances in practical applications such as desalination of sea water and purification of waste water. The basic technology is currently being further developed for the full utilization of sea water or waste water. This paper introduces a new method of evaluating desalination membranes, which uses instead of constant current polarization the potentiostatic polarization of membranes. A potentiostat with four electrodes, two reference electrodes and two electrolytic electrodes, has been constructed and applied to the evaluation of several membranes in commercial use. The optimum operation conditions for desalination membranes can also be estimated by using the four-electrode potentiostat. (Japanese)

Combind Forms of Magnesium and Nickel in Asbestos Tailings

T. Tanaka, S. Tasai, R. Shibayama
and S. Suzuki

Journal of the Mining and Metallurgical
Institute of Japan, **89**, 675 (1973).

Combined forms of magnesium and nickel in asbestos tailings from Hokkaido were determined by means of X-ray diffraction, thermobalance, differencial thermal analysis and electron probe microanalyzer. The serpentine mineral antigorite forms about 90 per cent of the tailings. Brucite associated with silicates is usually present. The content of MgO as brucite is about 10 per cent of the total magnesium oxide. The nickel is present in three forms: as a substitution for the magnesium in antigorite, as a sulphide identified as Ni_3S_2 and a hydroxide, Distribution of the nickel among these three minerals is estimated about 50, 30, and 20 per cent of the total nickel respectively. The chromium found in the magnetic fraction of the tailings is present as chromite. The concentration of this mineral into the magnetic fraction is attributed to the formation of magnetite at the surface of a chromite grain. (Japanese)

Electrochemistry of Surface Finishing of Metals

M. Nagayama

Bulletin of Japan Institute of Metals,
12, 679 (1973), No. 10.

The mechanism of typical surface finishing reactions was reviewed from the standpoint view of electrochemistry. Topics listed below were taken mainly from the research being conducted in the author's laboratory. (1) Copper plating from Cu-pyrophosphate solutions. (2) Chromium plating from chromic acid solutions containing sulfate. (3) Electropolishing (general). (4) Anodizing of aluminum in various acid solutions. (5) Chemical polishing, Chemical plating (general). Optimum conditions of these finishing procedures were explained in view of the qualities of the surface obtained, current efficiency and stability of the solution. (Japanese)

Electrochemistry in Metallic Corrosion

N. Sato

Bulletin of the Japan Institute of Metals,
12, 661 (1973), No. 10.

This review paper describes the electrochemistry of electric double layers formed at the interface between a metal and a solution, the kinetics of corrosion processes, the electrode potential of metals, the local cell model of metallic corrosion, the metallic passivation, and the corrosion product films on metals. Dry corrosion (high temperature oxidation) is also described in view of the local cell model, and experimental results given by C. Wagner, which prove the model, are reviewed. Attention is paid throughout the paper to the electrochemical concept that can be applied to understanding the mechanisms of corrosion and oxidation of metals. It is pointed out that, electrochemically, the anodic oxide formation in aqueous solution is half way between the wet corrosion and the dry oxidation. (Japanese)

Introduction to Corrosion and Its Prevention of Metallic Materials.

N. Sato.

Water Purification and Liquid Wastes Treatment,
14, 165 (1973), No. 2.

This lecture paper introduces to practicing water enginners the fundamental knowledge of metallic corrosion and its prevention in laymen's language to be understood by those who are not necessarily technically trained. The property of materials, the principle of metal corrosion, the anode and cathode of corroding metals, the electrode potential of metals in aqueous solution, the passivity of metals, the types of corrosion (homogeneous, galvanic, crevice, pitting, preferential parting, intergranular corrosion, and stress corrosion cracking), and the principle of corrosion prevention are discribed. The method of corrosion prevention is classified in the scope of corrosion mechanisms as follows: 1) Controlling the anodic reaction, 2) Controlling the cathodic reaction, 3) Controlling the ion transport in aqueous solution near metal surfaces, and 4) Controlling the electron conduction between the anode and the cathode. (Japanese)

An Introduction to Corrosion Science of Stainless Steels.

N. Sato

Chemistry and Industry (Kagaku to Kogyo),
26, 258 (1973), No. 5.

This paper explains in plain language why stainless steels resist corrosion. Describing the corrosion reaction and passivation of metals, the author illustrates the anti-corrosion property of stainless steels as resulting from formation of a very thin, unvisible corrosion product film on the metals. This film, often called the passive film, is produced when the environment contains oxidants capable of passivating the metals. The passive film is a kind of rust that suppresses further rusting. There is another kind of rust which accelerates further rusting, as one often observes with mild steels. For good stability and performance of stainless steels, therefore, one has to look at the property of the corrosion product film which depends not only on the alloy composition but also on the oxidants and aggressive ions in the environment. (Japanese)

Effect of Imperfection of Crystal Surfaces on Chemical Reactivity of Solids

T. Yamashina

The 4th Seminar on Thin Films and Surface
Physics, Text p. 10–1–10–33 (1973).

This review gives a general discription on the correlation between chemical reactivity and surface structure of solids. Progress in instrumental techniques for surface studies as well as in theories correlating the surface active sites with imperfections is included. Discussions cover geometrical and electronic factors of the active sites affecting the adsorption and catalytic activities of metals and alloys, especially of the clean surface of copper-nickel alloys as an example. (Japanese)