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For additional copies and more information, please write to the editors ;

Professor N. Sato, Electrochemistry Laboratory,
Professor K. Nishida, High Temperature Metal Chemistry Laboratory,
Professor T. Ishikawa, Electrometallurgy Laboratory.

Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8,
Kita-ku, Sapporo, 060, Japan

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ELECTROCHEMISTRY LABORATORY

Professor Dr. N. Sato, Assistant Professor Dr. K. Kudo,
Dr. M. Seo, Mr. M. Sakashita, and Miss C. Miura

Students

T. Ohtsuka, R. Nishimura, N. Arayama, R. Saito,
H. Goto, Y. Yomura, and K. Horino

Passivity of iron-group metals and alloys in aqueous solutions is at present the main subject of research in this laboratary. Details of the phase structure of passive oxide films on iron have continuously been obtained by means of ellipsometry as well as electrochemical analysis, and the film growth and aging are being studied in neutral and acidic solutions. The passive film on cobalt is being studied intensively and it was so far found that the film consists of an inner CoO layer and an outer Co_3O_4 layer which forms a barrier layer. Electrode impedance measurements of passivated iron and nickel in neutral and acidic solutions are also being carried out in comparison with the results obtained by ellipsometry.

In relation to the passivity study, development and imprevement of ellipsometric techniques are continuously being made to establish a high sensitive ellipsometer, ellipsometric spectrometer, and automatic ellipecmeter.

Membrane experiments are now extended from nickel hydroxide membranes to chromium hydroxide membranes and nickel-chromium and nickel-molybudinum hydroxide membranes, and the anionic and cationic transport property of these membranes are being made clear.

Beside these corrosion-related studies, a fuel cell catalysis experiment with hydrogen and hydrocarbon fuels in acid solutions was initiated this year by use of platiunm and some extremely corrosion-resistive alloys as electrode.

An international collaborative research program on the passivity of iron-base alloys between this laboratory and Professor Staehle's laboratory at the Ohio State University was officially approved for two years by JSPS in Japan and NSF in U. S. A. On this program, Professor Staehle visited this laboratory for three days in March and Dr. Lumsden for three weeks in Novemder. Professor Sato also visited the Ohio State University for two weeks in June, and Dr. Seo continued his stay there until September.

Two other of reign scientists visited this laboratory ; Dr. H. E. Freer, Department of Engineerng, the University of Leicester, England and Dr. W. M. H. Sachtler, Division of Inorganic Physical Chemistry, Shell Research Laboratory, Amsterdam, Netherlands.

Professor Sato and Dr. Seo attended the Gordon Research Conference on Corrosion held in New London, New Hampshire, U S A, and the NACE Annual Conference in Chicago in March where Dr. Seo presented a paper on Auger electron spectroscopy analysis of passive films on iron. Professor Sato visited Dr. Kruger's laboratory in N B S for two days and had a pleasure to see members of the Board of Trustees of the Federation of Materials Societies of U S A. in Washington. Dr. Seo had a short visit to N B S presenting a lecture on application of Auger electron spectroscopy to analysis of passive films on iron. He also visited Dr. Cohen's laboratory at N R C in Ottawa and presented a short talk on Auger electron spectroscopy analysis.

Dr. Kudo stayed for one year at Professor A. B. Winterbottom's laboratory and on his way back to Japan he visited the following laboratories ; Central Institute for Industrial Research in Oslo, Swedish Corrosion Institute in Stockholm, Corrosion Laboratory at Helsinki University of Technoloqy, Chemistry Laboratory in Technical University of Denmark, Institute of Physical Chemistry at Free University of Berlin, Laboratory of Solid State Physics in University of Paris, Westinghouse Research Laborantory in Brussels, Institute of Industrial Science at University of Leuven, Sir John Cass School of Science and Technology in London Polytechnic, Department of Physics at University of Waterloo in Canada, N B S, Corrosion Center at the Ohio State University, and Lawrence Berkeley Laboratory at University of California in U S A. During this trip, he presented a lecture at Westingouse Research Laboratory on application of ellipsometry to the study of metallic corrosion, and attended 15th Corrosion Science Symposium held at University of Cambridge to present a paper on his work done in Norway.

Oral Presentations

Characteristics of Nickel Hydroxide Membranes ; M. Sakashita and N. Sato : 9th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb., 1974.

Anodic Passive Films formed on Fe–Ni Alloys ; Y. Ohtake and N. Sato : *ibid.*, Feb,. 1974.

Transport of Water through Nickel Hydroxide Membranes ; M. Sakashita and N. Sato : 41st Annual Conference of the Japan Electrochemical Society, Apr., 1974.

Ellipsometry of Anodic Oxide Films on Cobalt ; T. Ohtsuka and N. Sato : *ibid.*, Apr., 1974.

Anodic Behaviour of Fe–Ni Alloys in Neutral and Acidic Solutions ; Y. Ohtake and N. Sato : Ist Annual Conference of the Japan Society of Corrosion Engineering, May, 1974.

Automatic Ellipsometry of Passive Oxide Films on Fe—The Method and Its Application ; R. Nishimura and N. Sato : *ibid.*, May, 1974.

NACE and Its Annual Conference '74 ; N. Sato : *ibid.*, May, 1974.

Recent Progress in Passivity of Metals ; N. Sato : Theme Symposium in the Japan Institute of Metals, June 1974.

Structure of Passive Oxide Films on Cobalt in Neutral Solutions ; T. Ohtsuka and N. Sato : Hokkaido Section Meeting of J I M, June, 1974.

Electrode Impedance of Anodic Oxide Films on Iron in Neutral Solutions ; N. Arayama, K. Kudo and N. Sato : *ibid.*, June, 1974.

Ellipsometric Intensity Measurements—Aplication to the Study of

Passive Oxide Films on Iron ; R. Nishimura, K. Kudo and N. Sato : *ibid.*, June, 1974.

Stress Corrosion Cracking of Metallic Materials ; N. Sato : Corrosion and Protection Committee in the Society of Materials Science, Japan, June, 1974.

Application of Ellipsometry to the Study of Corrosion ; K. Kudo : Invited Lecture at Westinghouse Research Laboratory—Europe, Brussels, Belgium, Sept., 1974.

Ellipsometry of Anodic Oxide Filmon Fe–Ni Alloys in Neutral Solutions ; K. Kudo and Y. Ohtake : 15th Corrosion Science Symposium, Cambridge, England, Sept., 1974.

Catalytic Activity and Exo-Electron Emission of Solids ; N. Sato : 31st Autumn Conference of the Japan Chem. Soc., Oct., 1974.

Anodic Oxidation ; N. Sato : Japan-USSR Seminar on Electrochemistry, Oct., 1974.

Anodic Behaviour of Cobalt—Thickness Measurements of Anodic Oxide Films by Ellipsometry ; T. Ohtsuka and N. Sato : 75th Autumn Conference of JIM., Nov., 1974.

Electrode Potential Dependence of the Compsition of Passive Oxide Films on Iron in Neutral Solution ; R. Nishimura, K. Kudo and N. Sato : *ibid.*, Nov., 1974.

The Latest Trend of Corrosion Research and Corrosion Loss Estimate in U S A ; N. Sato : 2nd Symposium of Corrosion and Protection, Nov., 1974.

Composition of Passive Oxide Film on Iron Depending on the Electrode Potenial and Oxidation Time; R. Nishimura, K. Kudo and N. Sato : Hokkaido Section Meeting of the Japan Electrochemical Society, Dec., 1974.

Electorde Impedance of Passive Oxide Films on Iron and Fe–Ni Alloys in Neutral Solutions ; N. Arayama, K. Kudo and N. Sato : *ibid.*, Dec., 1974.

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

A. Matsui, T. Tani, S. Murai, J. Fuzino, K. Kimura,
M. Takahashi, I. Maekawa, K. Taniguchi,
H. Kinoshita, and M. Murakami

The laboratory is investigating the dry corrosion (oxidation and sulfurization) of metals and alloys. The diffusion in metals and sulfides are also being investigated by means of solid couple and metallic vapor techniques on the background of the corrosion and protection researches. Furthermore, decomposition of metal carbides and hydration of magnesium oxide in a wet atmosphere are also being studied.

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

(1) Oxidation of Co-based Ni alloys ; The oxygen pressure dependnce of the corrosion rates was measured and then nickel distribution in the (Co, Ni) O scale formed was analyzed by application of Wagner's new theory.

(2) A quasi binary FeS–MnS system; A quasi FeS–MnS phase diagram was constructed in the temperature and sulfur pressure ranges of 800–1100°C and 10^{0}–10^{-7} atm and the kinetics and scale structure of Fe–Mn alloys in sulfurization are also being clarified.

(3) Carburization of Fe-based Mn alloys ; The effect of third elements in the alloy on the diffusion of carbon was experimentally determined and also theoretically analyzed.

(4) Metallizing of refractory metals and their oxidation behaviors ; The oxidation behavior of the calorized Ta showed significant differences depending on corrosion temperatures (900–1300°C). Calorizing of Mo and Zr is also done.

(5) Diffusion phenomena of Fe-group metals with Sb and Zn ;

Ni metal is penetrated with Sb and Zn vapor. In this case Sb or Zn is a diffusing species in Ni metals.

(6) Application of light beam melter to crystal growth ; The modified light beam melter possesses an ability of max. 3,000°C and is used for a study on a Ta_2O_5–Al_2O_3 system.

Oral Presentations

Anti-oxidation Properties of Calorized Ta sheet —(I)— (Calorizing of Ta sheet) ; M. Hachinohe and K. Nishida : The 9th Annual Meeting of Corrosion Research Association in Hokkaido, Feb., 1974.

Growth of Iron Sulfide during Sulfurization of Pure iron ; K. Nishida and T. Narita : ICCG–4th (Tokyo), March, 1974.

On the Cation Distribution in the Oxide Scale formed on Co–Ni Alloys ; T. Narita and K. Nishida: The Spring Meeting of the Japan Institute of Metals, Apr., 1974.

Self-diffusivities of Different Metal Atoms in FeS Scale ;T. Narita and K. Nishida : *ibid.*, Apr., 1974.

Calorizing of Ta Sheet and Their Oxidation Phenomena ; K. Nishida and M. Hachinohe : '74 Spring Meeing of Corrosion and Protection Engineering, May 1974.

Hydration of Fume of Magnesium Oxide ; K. Atarashiya : The Annual Meeting of the Ceramic Soc. Japan, May, 1974.

Thermodynamics of a Quasi FeS–MnS Binary System —(I)— ; T. Tani, T. Narita and K. Nishida : The Hokkaido Section Meeting of JIM and ISIJ, July, 1974.

Oxidation Behavior of Co–Ni Alloys ; T. Narita and K. Nishida : *ibid.*, July, 1974.

High-Temperature Oxidation of Co–Ni Alloys —(I)— Analysis of the Cation Distribution in the Oxide Scale ; T. Narita and K. Nishida : The Fall Meeting of Japan Institute of Metals, Nov., 1974.

The Sulfur Pressure Dependence of a Quasi FeS–MnS Binary Phase Diagram ; T. Tani, T. Narita, and K. Nishida : ibid., Nov., 1974.

Some Problems on the High-Temperature Oxidation of Alloys ; T. Narita and K. Nishida : The Hokkaido Section Meeting of JIM and ISIJ, Nov., 1974.

Some Considerations of Sulfurization of Metals and Alloys at High-Temperature ; T. Narita and K. Nishida: The Hokkaido Section Meeting of the Japan Electrochem. Soc.,Dec. ,1974.

ELECTROMETALLURGY LABOLATORY

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

Students

S. Tamagawa, Y. Karikome, K. Sato, M. Konno,
O. Yamamoto, T. Abe, A. Imai, N. Ozaki,
and S. Nishiuchi

Research subjects in this laboratory are as follows.

(1) Concerning low temperature electrorefining of aluminum in the molten salt mixtures of aluminum chloride and alkali chloride, the mechanism of cathodic deposition of solid aluminum and morphological properties of the deposited metal are being clarified using rotating cylindrical cathode by means of chronoamperometry, chemical analysis and surface observation *in situ.* Labolatory scale tests for electrowinning of liquid aluminum are also being carried out in these melts at 700°–800°C.

(2) Electrodeposition of iron and hydrogen in acidic ferrous sulfate 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 bipolar electrolysis of mercurous nitrate solution are also in progress.

(3) The corrosion rates of iron, steel and copper under various heat transfer conditions are being determined at various temperatures by colourmetric analysis. Effects of heat transfer on pitting corrosion behaviour of stainless steel and of aluminum are being clarified in ferric chloride and sodium chloride solutions.

Oral Presentation

Fundamental Study on Heat Transfer Corrosin of Iron and Copper ; M. Asakawa and T. Ishikawa : The 9th Annual Metting of the Corrosion Research Association in Hokkaido, Feb. 1974.

Rate of Electron Transfer Step of Hydrogen Evolution Reaction on Gold in Acid and Alkaline Solutions ; T. Sasaki and A. Matsuda : The 41st Annual Meeting of the Electrochemical Society of Japan, Apr., 1974.

Some Electrochemical Methods for Evaluation of Localized Corrosion of Passive Metal ; T. Ishikawa : The 12th Seminar on Corrosion and Protection, Electrochemical Society of Japan, Apr., 1974.

Effects of Temperature, Anion and Heat-transfer on Corrosion Rate of Copper ; M. Asakawa, T. Ishikawa and R. Midorikawa : The Spring Meeting of Japan Society of Corrosion Engineering, May, 1974.

Effect of Heat-transfer on Pitting Corrosion of 18–8 Stainless Steel; M. Konno and T. Ishikawa : The Hokkaido Section of J. I. M. and I. S. I. J., June, 1974.

Surface Oxide Films on Metals in Fused Salts ; T. Ishikawa : Hokkaido Section Seminar on Passive Film, Japan Institute of Metals, July, 1974.

Corrosion Behavior of Metals in Fused Salts —On the Similarity to Higher Oxidation and Passivity— ; T. Ishikawa : The 67th Meeting on Fused Salt, Electrochemical Society of Japan, Nov., 1974.

Influence of Zinc and Cadmium Ion on Cathodic Deposition of Iron ; Y. Karikome and T. Ishikawa : 1st Hokkaido Section Meeting of Electrochemical Society of Japan, Dec., 1974.

PHYSICAL METALLURGY LABORATORY

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

Students

T. Nakai, S. Ishiyama, M. Kobayashi, T. Takahashi,
M. Uetsuka, S. Kikuchi, N. Yokoya, T. Sawada,
S. Ohnuki, T. Niiyama, and M. Kurita

Main research activities of this laboratory are concerned with the aging phenomena of iron alloys, and the interaction between the solute atoms and the points defects which are produced by the high voltage electron irradiation or neutron irradiation. Also the stress corrosion cracking of stainless steels is investigated. Some projects in progress are listed as follows:

1) Effect of the electron irradiation on aging phenomena of iron alloys. Solute atoms, such as carbon and nitrogen, interact with point defects produced by electron irradiation using 650 kV electron microscope, resulting in retardation of precipitation. Al base alloys are also investigated.

2) Effect of neutron irradiation on mechanical properties of bcc metal alloys. Influence of defects clusters and voids produced during neutron irradiation on strength and deformation structures is investigated by using JMTR.

3) Dynamical behavior of the serrated flows in the work-hardening region. A relation between the dislocation motion and dynamic deformation band propagation is investigated, which is compared with the behavior of Lüders band propagation.

4) Effect of molybdenum on stress corrosion cracking of stainless steel is analysed by using the high speed straining electrode method. Addition of Mo is found to decrease the anodic activity of fresh surface and to facilitate the decay of anodic activity due to repassivation in boiling magnesium chloride solution. Combin-

ation of the above two factors is concluded to cntrol the susceptibility of these steels to SCC.

5) Surface phenomena at hydrogn charging of pure iron are studied. Blistering is found to have a relation with the intergranular cracking under the surface, but not with the embrittlement of bulk iron. Irregular change in hardness with charging is being investigated.

6) Multichannel apparatus for measuring the pitting potential has been developed: the apparatus consists of one potentiostat and multichannel loops connecting with each of 12 specimens. Pitting potential at a constant sweep velosity of the potential and/or the induction time at a constant potential can be measured for 12 specimens at the same time. Statistical nature of pitting phenomena is investigated.

Oral Presentations

Break Down and Reformation of the Surface Films; T. Shibata: Symposium on Stress Corrosion Cracking, The Japan Institute of Metals, Jan. 1974.

A Method for Determination of Anodic Activity of Metal Surface; T. Shibata and T. Takeyama: The 9th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb. 1974.

Aging Phenomena and Defects Produced by High Voltage Electron Microscope; T. Takeyama, H. Takahashi, Y. Sato and S. Mochizuki: The Hokkaido Section Meeting of Japan Society for Electronmicroscopy, Feb. 1974.

Behavior of Carbon Atoms and Point Defects Produced by Electron Irradiation of Iron (II); H. Takahashi and T. Takeyama: The Spring Meeting of the Japan Institute of Metals, Apr. 1974.

The Effect of Plastic Deformation on Anodic Reactivity of Pure Iron; T. Shibata and T. Takeyama: *ibid.*, Apr. 1974.

The Effect of Rolling Reduction on Mechanical Properties of Mild Steel in the Process of Recovery and Recrystallization; H. Uetsuka, H. Takahashi and T. Takeyama: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and

Steel Institute of Japan, Jun. 1974.

The Observation of Neutron Irradiated Fe–C Alloys by Transmission Electron Microscopy; H. Takahashi, T. Takeyama, K. Konno and H. Kayano: *ibid.*, Jun. 1974.

Relation between the Nature of the Passive Film of Stainless Steel and its Resistance to Corrosion; T. Shibata: The Tohoku Section Seminar on Passive Film, The Japan Institute of Metals, Jun. 1974.

On the Measurement of Pitting Potential; T. Shibata: The 9th Committee of Japan Society of Corrosion Engineering, Jul. 1974.

The Effect of Carbon on the Annealing of High Voltage Electron-Irradiated Iron; T. Takeyama and H. Takahashi: The 8th International Congress on Electron Microscopy, Aug. 1974.

The Effect of Electron-Irradiation on Aging Phenomena of Fe–N Alloys; H. Takahashi and T. Takeyama: The Fall Meeting of the Japan Institute of Metals, Nov. 1974.

Plastic Deformation and Anodic Reactivity of Stainless Steels; T. Shibata, M. Kobayashi and T. Takeyama: Symposium on the Mechanisum of SCC of Austenitic Stainless Steels, Iron and Steel Institute of Japan, Nov. 1974.

Hydrogen Embrittlement of Pure Iron; S. Kikuchi, T. Shibata and T. Takeyama: The Hokkaido Section Meeting of the Japan Institute of Metals and Iron and Steel Institute of Japan, Nov. 1974.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Mr. H. Tamura,
Dr. H. Takahashi, Mr. H. Konno,
and Mr. Y. Otake

Students

K. Takahashi, M. Koda, Y. Sato,
Y. Tsuneta (Miss), and T. Ujiye

Research being conducted in this laboratory is connected to the anocdi oxidation of metals in aqueous solutions and to the cathodic deposition of metals from solutions of chelates. Mechanism of air-oxidation of metals has been a matter of interest and various methods of analysis of metal ions in aqueous solutions are being developed. Investigation of the composition profiles of oxides is being planned by utilizing an ESCA apparatus which will be set up somewhere in the Faculty by the aid of the Ministry of Education of Japan.

Topics of present research are asfollows:

(1) Formation and dissolution characteristics of porous anodic oxide films on aluminum. Investigation of the dissolution behavior of the oxide is being continued in various acid solution with and without applied voltage. Transport numbers of Al^{3+} and O^{2-} ions across the barrier layer during anodizing have been determined for solutions of various acids by the method proposed by Middelhoek.

(2) Pore-filling of porous anodic oxide films on aluminum. This phenomenon can be observed when the specimen covered with porous oxide is reanodized in a neutral borate solution at a constant current density. Porosity of oxide films is being measured by utilizing this phenomenon.

(3) Sealing of porous anodic oxide films on aluminum. Hydration process occurring at the pore-wall and the barrier layer when oxide film is treated with hot water has been examined as function

of the anodizing voltage and temperature of the acid electrolyte used.

(4) Deposition of copper from copper-pyrophosphate solutions. The cathodic polarization curves has been measured as functions of temperature, solution compsition and pH. The adsorption of pyrophosphate ions on the surface of the specimen and the effect of addition of NH_3 is being investigated using XMA.

(5) Air-oxidation of ferrous ion in neutral solution. Effect of iron (III)-hydroxide, the reaction product, on the reaction rate is being examined. The method of analysis of ferrous ion in the presence of a large amount of Fe^{3+} has been developed. Adsorption of Fe^{2+} on iron (III)-hydroxide is being measured as a function of pH in the presence of various anions.

Oral Presentations

Rate of Oxygenation of Ferrous Ion at High Concentrations ; H. Tamura, K. Takahashi and M. Nagayama : The 1974 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Anal. Chem. and the Japan Chem. Soc., Jan. 1974.

Spectrophotometric Determination of Al with Ferron—Decompsition of Mn-Ferron Complexes by EDTA ; K. Goto, H. Tamura, Y. Sato and M. Nagayama, *ibid.*, Jan. 1974.

Sealing of Porous Anodic Oxide Films on Al Formed in an Oxalic Acid Solution ; H. Takahashi, M. Koda and Magayama : *ibid.*, Jan. 1974.

Structural Change of Porous Anodic Oxide Films on Al during Initial Periods of Anodizing ; H. Takahashi and M. Nagayama: The 9th Annual Meeting of the Corrosion Research Association in Hokkaido, Mar. 1974.

Effect of Iron (III)-Hydroxide on the Rate of Oxygenation of Ferrous Ion ; H. Tamura, K. Takahashi and M. Nagayama : The 41st Annual Meeting of the Japan Electrochem. Soc., Apr. 1974.

Mechanism of Formation of Porous Anodic Oxide Films on Al during Initial Periods of Anodizing ; H. Takahashi and M.

Nagayama: *ibid.*, Apr. 1974.

Activation Energy and Mechanism of Copper Plating Reaction in Cu-(II)-Pyrophosphate Solution; H. Konno and M. Nagayama: *ibid.*, Apr. 1974.

Estimation of Corrosion Rate by Polarization Measurement; The 12th Seminar on Corrosion and It's Protection sponsored by Japan Electrochemical Society, Apr. 1974.

Mechanism of Pore-Filling Phenomena during Anodizing of Al Covered with Porous Aneic Oxide Films in a Neutral Boric Acid-Borate Solution; H. Takahashi and M. Nagayama: The 49th Meeting of the Metal Finishing Soc. of Japan, May 1974.

Electron Microscopy of Porous Anodic Oxide Films on Al by Ultra-Thin Sectioning Technique. III. Structural Change of Films during Open-Circuit Dissolution; H. Takahashi, M. Nagayama and H. Akahori: The 30th Annual Meeting of the Japan Society for Electron Microscopy, May 1974.

Formation of Anodic Oxide Films on Al; M. Nagayama: Symposioum sposnored by the Japan Institute of Metals, July 1974.

Transport Numbers of Al^{3+} and O^{2-} Ions across Anodic Oxide Films on Al during Their Formation; H. Takahashi and M. Nagayama: The 1974 Summer Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem. July 1974.

Treatment of Waste Water in Hokkaido University; M. Nagayama, Seminar sponsored by the Hokkaido Section of the Japan Anal. Chem. Soc., M. Nagayama: Aug. 1974.

Measurement of Porosity of Anodic Oxide Films on Aluminum by Electrochemical Technique; H. Takahashi and M. Nagayama: The 50th Meeting of the Metal Finishing Soc. of Japan, Nov. 1974.

Role of Coexisting Anions in the Oxygenation of Ferrous Ion in Neutral Solution; H. Tamura and M. Nagayama: The 1974 Meeting of the Hokkaido Sections of the Japan Electrochem. Soc., Dec. 1974.

Proper Conditions of Copper Plating from Copper Pyrophosphate

Solutions and Structure of Deposit ; H. Konno and M. Nagayama : *ibid.* Dec. 1974.

Estimation of the Geometrical Structure of Porous Anodic Oxide Film on Al by Pore-Filling Method ; H. Takahashi and M. Nagayama : *ibid.* Dec. 1974.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

T. Nagasawa, K. Matsushita, K. Igarashi, A. Ando,
H. Motoki, A. Aoki, A. Onodera, H. Kawamoto,
H. Koguchi, and Y. Sugawara

Current activities in this laboratory are on the rupture strength of cast irons, the growth mechanism of cast iron at elevated temperature, and the failure analysis of machine members. Some researches of SEM fractography were carried out on the growth of cast iron and the temper brittleness of steel.

Results are summarized as follows:

(1) A new formula for the estimation of bending strength of cast iron from tensile strength was introduced theoretically and proposed as $\sigma_b = (2.0 - \sigma_t/100)\,\sigma_t$, where σ_b and σ_t are the bending and the tensile strengths in kg/mm^2, respectively. This formula of simple form can be used for application and gives a safer value than others proposed formerly.

(2) For the paper "On the rupture strength of notched cast iron." published Jan. 1973 the Kobayashi's Memorial Prize was given by The Japan Foundrymen's Society. After that the research "On the rupture strength of deep notched cast iron." was published. In this paper the effect of outer artificial notches and inner notches of graphite flake on the rupture strength was discussed.

(3) Strength of T-beam made of cast iron was analyzed by calulation with a computer and tested experimentally. Effect of ribs on the strength of beam gives useful data for the designing of castings.

(4) In order to examine the effect of air in heating atmosphere

on the growth of cast iron, growth tests were carried out in mixed gases of argon and air with various concentrations. A remarkable increase of growth that occurs at low concentrations of air was explained by a concept of self-carburizing within heated cast iron, which was based on the growth mechanism of graphite migration.

(5) SEM fractography of grown cast iron was carried out and the result obtained showed very interesitng features of fine graphite redistributed and voids fomed around graphite nodules. XMA analysis of a carbon, silicon and oxygen at the same position as observed with SEM showed clearly that the growth of cast iron is not due to oxidation but to irreversible migration of graphite.

(6) To analyze the cause of machine accidents the mechanical-and-metallurgical approach of failure analysis was applied. Serious practical failures occured recently were a falling of builling-roof by bucking of truss members, a hammer accident of piling machine by abrasion of lifting member, and a break down of automobile bolts by metal fatigue.

Oral Presentations

Recent Progress of Foundry Industry in Hokkaido ; K. Nagaoka ; The General Lecture Meeting on Foundry, June 1974.

Rupture Strength of T-Beam made of Cast Iron ; T. Noguchi ; The Grand Lecture Meeting of The Society of Material Science, Japan, May 1974.

The Effect of Ribs on the Bending Strength of Cast Iron T-Beam ; T. Noguchi and K. Nagaoka : The 85th Grand Lecture Meeting of The Japan Foundrymen's Society, May 1974.

Effect of Oxygen Concentration in Atmosphere on the Growth of Cast Iron ; M. Sōma and K. Nagaoka, The 85th Grand Lecture Meeting of The Japan Foundrymen's Society, May 1974.

Machine Accidents and Safety ; K. Nagaoka ; The Lecture Meeting on Safety, June 1974.

Acceleration of Growth in Cast Iron by CO Atmosphere ; M. Sōma and K. Nagaoka ; The Hokkaido Section Lecture Meeting of The Japan Foundrymen's Society, June 1974.

SEM Observation on the Growth of S. G. Iron; M. Sōma and K. Nagaoka, The 86th Grand Lecture Meeting of The Japan Foundrymen's Society, Oct. 1974.

NUCLEAR REACTOR MATERIALS LABORATORY

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

Studeuts

K. Fujinaga, H. Narita, H. Hayashi, M. Inatani,
S. Kato, N. Shindo, H. Takai and M. Makita

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

(1) Hydrogen uptake in titanium and other metals: The kinetic studies of the hydrogen uptake into the hydride-forming metals and alloys were made by using the vacuum technique and the nuclear chemical method. The specimens used in these studies were titanium, zirconium, their alloys so-called AB_3-alloys and others. Among these metals, the materials of the hydrogen reservoir are included.

(2) Application of Mössbauer spectroscopy to corrosion research: The rate of oxidation of the pure iron foil were measured both in air and dry steam by using the Mössbauer spectroscopy and the thermogravimetry. Various oxidation products were identified and quantified by analysis of the Mössbauer spectra. Also, various kinds of oxides, hydroxides and oxy-hydoxides of iron were synthesized and treated under various conditions, and the Mössbauer spectra of these compounds were measured.

(3) Oxidation of uranium dioxide: Thermogravimetric study of the oxidation of UO_2 into U_3O_8 was continued since last year. The effect of the heating condition on the oxidation behavior especially attracts our attention. Also, the dissolution rate of the

oxidation products of UO_2, which was oxidized to various extent, was measured in aqueous solutions of nitric acid.

(4) A plan of study which aims at the clarification of the effect of various kinds of surface treatment on the corrosion of zirconium and its alloys is under consideration.

Oral Presentations

Effect of Calcination on Structure and Chemical Reactivity of γ-Ferric Oxyhydroxide ; H. Goto, H. Ohashi, K. Hirohara and T. Morozumi : The 1974 Winter Meeting of the Hokkaido Sections of the Japan Anal. Chem. Soc. and the Japan Chem. Soc., Jan. 1974.

Study on Oxidation of Steel by the Mössbauer Spectroscopy, Preliminary Report ; H. Ohashi, M. Koizumi and T. Morozumi : The 9th Annual Meeting of the Corrosion Research Association in Hokkaido, Feb. 1974.

Automatic Continuous Analysis of Ozone in Working Area of Electron Linear Accelerator by Controlled Potential Iodometry ; H. Ohahi, H. Nagashima, T. Suzuki and T. Morozumi : The 1974 Annual Meeting of the Atomic Energy Society of Japan, March 1974.

The Stopping Power of Metal Hydrides against the 20~100 keV Deuteron ; T. Mizuno, K. Fujinaga and T. Morozumi : *ibid.*, March 1974.

Reaction between γ-Ferric Oxyhydroxide and the Potentiostatically Controlled I^-–I_3^- Redox System ; H. Ohashi, H. Goto, K. Hirohara and T. Morozumi : The 41th Annual Meeting of the Electrochemical Society of Japan, Apr. 1974.

Rate Law of Hydride Formation on Titanium Surface by Cathodic Polarization ; T. Mizuno, M. Nishida and T. Morozumi : *ibid.*, Apr. 1974.

Study on the Structual Change of Calcined γ-Ferric Oxyhydroxide by the Mössbauer Spectrometry ; H. Ohashi, and T. Morozumi : The 1st Annual Meeting of the Hokkaido Section of the Electrochemical Society of Japan, Dec. 1974.

The Change of Lattice Parameter of Titanium Surface Covered with Hydride by Cathodic Polarization; T. Mizuno and T. Morozumi: *ibid.*, Dec. 1974.

VACUUM SCIENCE LABORATORY

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

Students

T. Abe, T. Sasaki, F. Tanuma and Y. Miura

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 catalytic activity for 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 and self-sustained electron emission form tin oxide films are also being made.

Oral Presentations

Preparation of iron nitride films by means of reactive sputtering method; Y. Kaku, S. Tanaka, T. Abe and T. Yamashina: The Hokkaido Section Meeting of Japan Chemical Society, Sapporo, Jan. 1974.

Preparation of nitride films of molybdenum and titanium; T. Abe T. Hanasaka and T. Yamashina: *ibid.*

Measurement of water adsorption over anodic oxide film on aluminum; S. Matsumura, M. Nagasaka and T. Yamashina: ibid.

Electron emission from vacuum evaporated tin oxide films; T. Hanaska, T. Satake, M. Hashida and T. Yamashina: The 6th Internationa Vacuum Congress, Kyoto, Mar. 1974.

Sorption kinetics of hydrogen and deuterium at low pressures by titanium and zirconium; M. Nagasaka and T. Yamashina: ibid.

Effect of argon ion-bombardment on and exchange reaction of hydrogen by evaporated nickel films; K. Watanabe and T. Yamashina: The 2nd International Conference on Solid Surfaces, Kyoto, Mar. 1974.

A study of catalytic activity factors on clean surface of copper-nickel alloys; Y. Takasu and T. Yamashina: *ibid.*

Structure and adsorption characteristics of porous vycor glass—an application of positronium annihilation method; Y. Itoh, M. Nagasaka and T. Yamashina: The 30th Annual Meeting of the Japan Chemical Society, Osaka, Apr. 1974.

Chemical reactivity and structure iron nitride films (Fe_xN) prepared by reactive sputtering; Y. Kaku, S. Tanaka, T. Abe and T. Yamashina: *ibid.*

A consideration of catalytic activity factors on copper-nickel alloys; Y. Takasu, Y. Matsuda and T. Yamashina: *ibid.*

Self-sustained emission of electrons from tin-oxide films; T. Satake, M. Hashiba, T. Hanasaka and T. Yamashina: ibid.

Oxidation of metals and structure of oxide films under very low pressures of oxygen; T. Yamashina: Research Meeting of Japan Institute of Metals, Muroran, July. 1974.

Low pressure sorption of nitrogen over zirconium at elevated temperatures; M. Nagasaka and T. Yamashina: The 15th Annual Meeting of Vacuum Society of Japan, Kyoto, Nov. 1974.

A consideration on deposition rate of metallic thin films in the process of reactive sputtering; T. Abe and T. Yamashina: *ibid.*

ESR spectra form oxygen on reactive-sputtered silver oxide films; S. Tanaka and T. Yamashina: The 35th Discussion Meeting of Japan Catalysis Society, Sendai, Oct. 1974.

Thermal desorption of formic acid from the surface of iridium and tungsten; K. Watanabe and R. S. Hansen: *ibid.*

NONFERROUS EXTRACTION METALLURGY LABORATORY

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

Students

K. Harashima, J. Iwahara, T. Iwazaki, F. Saishu,
N. Yamazaki and M. Hosokawa

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) Reduction kinetics of metal sulphides by hydrogen.

This study is aimed at finding the mechanism of direct reduction of sulphide ores. Observations of the nucleation and growth of reduced metals by scanning electronmicroscope, morphologic characteristics of the metals reduced from sulphides, oxides, chlorides and sulphates, and vapour phase reduction of metal sulphides are being made.

(2) 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.

(3) 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.

(4) 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 measurement of sulphides and metal electrodes in an autoclave under the conditions of temperatures up to 200°C and pressures of $50\mathrm{kg/cm}^2$.

Oral Presentations

Metal growth occurring in the hydrogen reduction of metal sulphides; T. Tanaka and R. Shibayama: The Meeting of Crystal Growth, Tokyo, Feb. 1974.

Extraction metallurgy of sulphide ores and hydrogen; T. Tanaka: The Meeting of the Corrosion Research Association in Hakkaido, Sapporo, Feb. 1974.

Researches on the pretreatments of copper concentrates by hydrogen; R. Shibayama, N. Katagiri and T. Tanaka: Annual Meeting of the Mining and Metallurgical Institute of Japan, Tokyo, March 1974.

Kinetic study on the reduction of germanium sulphide by hydrogen; H. Kiuchi, K. Harashima and T. Tanaka: *ibid.*, March 1974.

Fundamental studies on the pressure leaching of pyrite (7th Report); T. Nagai, H. Kiuchi, K. Harashima and J. Iwahara: *ibid.*, March 1974.

Characteristics of metals reduced from sulphides in hydrogen; R. Shibayama and T. Tanaka: The Hokkaido Section Meeting of the Japan Institute of Metals and the Iron and Steel Institute of Japan, Sapporo, June 1974.

Thermochemical splitting of water by metal sulphides and uses of hydrogen in the metallurgical treatments of sulphide ores; T. Tanaka: The 4th Meeting of Metallurgy Group, The Hokkaido Branch, The Mining and Metallurgical Institute of Japan, Sapporo July 1974.

Uses of hydrogen in hydrometallurgy; T. Nagai: *ibid.*, July 1974.

Conversion of hydrogen sulphide to hydrogen by molten lead; H. Kiuchi and T. Tanaka: The 1st Symposium on Hydrogen Energy System, Hydrogen Energy System Society, Tokyo, Nov. 1974.

Reaction between ferrous sulphide and water vapour at high temperature and thermal decomposition of ferrous hydroxide; R. Shibayama and T. Tanaka: *ibid.*, Nov. 1974.

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

H. Takahashi and T. Takeyama

Trans. Japan Inst. Metals, **15,** 357 (1974)

The present work was concerned with an experimental study of a Lüders band propagation in the blue-brittleness range and its analysis of some parameters, that is, dislocation structure, stress dependence of the band propagation velocity, and others. The specimen used was an α-iron containing 0.006 wt % carbon. A 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 $8 \times 10^9/\mathrm{cm}^2$ in the temperature range from 160 to 250°C. The magnitude of the stress drop did not directly depend on the amount of dislocations generated and its multiplication rate, but on the width of the Lüders band propagated. The propagation velocity of the 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, the initial velocity of the Lüders propagation increased: about 55.6 cm/sec at 160°C, 312.4 cm/sec at 200°C, and 595.5 cm/sec. This temperature dependence of the velocity could mainly be associated with that of the stress concentration factor caused by the dynamical strain aging near the Lüders band front. (English)

Effect of Electron Irradiation on the Precipitation Phenomena of a Fe–C Alloy

T. Takeyama and T. Takahashi

J. Japan Inst. Metals, **38,** 138 (1974)

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 and the examined with the electron microscope operated at 350 kV which did not exceed the threshold value of iron. The specimens aged below 240°C showed no visible precipitates in the irradiated area, but many small ε-carbide or cementite particles were observed in the non-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 (V : vacancy), resulting in the suppression of the carbide precipitation. The dissociation of the C–V pair and the precipitation of the cementites in the irradiated area were observed at temperatures 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 contribute to the nucliation and/or the growth of the cementite. Furthermore, the vacancies 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. (Japanese)

On the Tensile Rupture Strength of Notched Cast Iron

T. Noguchi

BISI 12237 (BISITS translation) 1974 April

The rupture strength of notched materials has been one of the most important problems in material engineering. In many works so far, this problems has been elucidated mainly on steels and other ductile metals, but little on cast iron. Grey cast iron generally containes many graphite flakes which act as micro-defects in the matrix. Consequently, the mechanical behavior of cast iron differs from that of ordinary ductile metals. Experiments were carried out on the notch strength of FC 25 class cast iron, using notched plate tensile specimens, and stress distribution was analyzed with the finite element method. Rupture strength decreased when the notch sharpness increased but tended to become constant at about $\rho<0.5$ mm. The stress analysis by the F. E. M. for the blunt notch ($\rho=10$, 15 mm) showed that the notched specimen ruptured when the maximum stress under the notch reached the tensile strength of cast iron. Thus, the criterion that the average stress of notch section is constant was not valid. The maximum stress criterion is shown to be valid, and rupture strength may be influenced by stress gradient. Strength saturation in the sharp notch region is throught to be due to graphite fiakes. (English)

A New Formula for the Estimation of Bending Strength of Cast Iron from Tensile Strength

T. Noguchi and K. Nagaoka

IMONO, **46,** 7 1974, July

In cast iron the value of the bending strength obtained from the rupture moment and section modulus of the beam is twice as large as the tensile strength. This is mainly due to the calcualtion based on the elasticity, while cast iron does not behave elastically. So far some empirical formulas were proposed to relate the tensile strength to the bending strength for the benefit of designing machine members with cast iron. Revising Nakanishi's theoretical equation the authors introduced a new formula of $\sigma_b = (2.0-\sigma_t/100)\sigma_t$, where σ_b and σ_t are the bending and the tensile strength in kg/mm^2, respectively. The formula gives an average value in the scattering of the bending strength obtained in authors' experiment. Mackenzie's equation gives higher value of bending strength, and Auguss's and Schneidewind's equation lay between the authors' and Mackenzie's. The authors' formula is very simple and can be used easily for application. It shows that the bending/tensile strength ratio is lowered with an increase of tensile strength. Furthermore in estimating the bending strength from the tensile strength the new formula gives a safer value than others. (Japanese)

Element Analysis of Grown Flake Graphite Cast Iron

M. Sōma

Hitachi Technical Data, SEM No. 8 (1974)

In order to elucidate the growth mechanism of cast iron heated in oxidizing atmosphere, an analysis of element-distribution was tried on carbon, silicon and oxygen with XMA equiped in SEM. Sample used was a grown flake graphite iron heated in CO_2 repeatedly 15 cycles between 600°C and 950°C. The image of secondary electron showed a SEM microstructure of grown flake cast iron with thorny protuberacnes from the surface of flake. The image of characteristic X-ray $C\text{–}K_\alpha$ showed carbon distribution within the flake and around it. The carbon analyzed around the graphite flake is graphite redistributed through the cyclic heating. Furthermore, an identical distribution of silicon and oxygen analyzed with XMA showed a formation of silicon oxide distributed around graphite flake especially in the thorns springed from the surface. A trial of XMA-analysis equiped in SEM on element distribution in grown cast iron gave a very important method for examination of the growth mechanism in cast iron. (Japanese)

On the Rupture Strength of Deeply Notched Cast Iron

T. Noguchi and K. Nagaoka

IMOTO, **46,** 9 (1974), Sept.

Rupture strength of cast iron was tested with plate specimens notched deeply on both sides. Root radius, depth of notch and width of plate were changed. Results were analyzed by the calculation of the stress distribution at the notch section. The rupture strength decreased until the notch radius decreased below 0.5 mm, and reached to a minimum constant strength which was about 70% of the unnotched rupture strength. For specimens of sharp notch ($\rho=0.06$ mm), NSR (notched rupture strength/unnotched rupture strength) decreased with increasing C/W (depth of notch/width of plate) to the minimum constant value of 0.7 in the region of C/W=0.2～0.7 and increased again over 0.7 of C/W. Experimental results on NSR changes were analyzed well with the stress concentration factors at the distance of 1.0～1.5 mm from the notch root. In cast iron the size of 1.0～1.5 mm is equivalent to the size of one or a couple of eutectic cell. The fracture toughness of cast iron was almost constant in the region of C=5～20 mm, but showed lower values in the outside of this region. These results suggest that the deep-notch strength of cast iron is affected remarkably by the stress distribution around the notch root. The fracture does not initiate directly from graphite flake but propagates with some plastic zone and micro-fracture within the region of 1.0～1.5 mm from the notch root. (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

Journal of the Japan Institute of
Metals, **38**, 688 (1974)

Co–Ni alloys over the whole composition range were oxidized in the temperature range from 1000 to 1200°C under 1 atm of pure oxygen, and kinetics, internal oxidation, surface morphology, and concentration profiles in the cross-section were clarified by means of thermogravimetry, X-ray diffraction, optical microscopy, and electron probe microanalysis. Results obtained are as follows: (1) The grown oxide was mainly the solid solution of CoO and NiO, except for the precipitation of Co_3O_4 particles in high Co–Ni alloys. (2) In all cases, NiO and CoO were found to concentrate in the alloy-scale and scale-gas interfaces, respectively. (3) Concentration profiles in the scale and an alloy substrate were shown by one mater curve at a specified temperature when the concentration was plotted against $x/\sqrt{t}$. This result shows that the concentration profiles are determined by the diffusion process in both of the scale and the alloy. (4) Internal oxidation and Co-depletion in the alloy substrate were found in the nickel-rich alloys, resulting in the enrichment of CoO in the scale. The growth rate of the Co-depletion zone depended not on the alloy composition but on the temperature. From the results of the present and other authors' studies the composition-temperature diagram of the oxidation behaviors was schematically shown. (Japanese)

The Preferred Orientation of the Ferrous Sulfide Scale on Pure Iron at 700°C

T. Narita and K. Nishida

Transactions of The Japan Institute of
Metals **15**, 314 (1974)

The preferred orientation and its variation with sulfur pressure were observed in the course of the study on the sulfurization of pure iron at 700°C. Further, SEM observations revealed the characteristic variation of the surface morphology of the scale with sulfur pressure. The preferred orientation of the grown scale changed with sulfur pressure and the orientation differences were quantitatively determined by means of X-ray pole figures. By using the diffusion theory as well as the present observations the effect of the preferred orientation of the scale on the overall corrosion rates was disclosed. The calculated value of $1/n$ as a measure of the pressure dependence of the corrosion rates is about 1/5.7. This value suggests that there is no interaction between vacancies and positive holes in the ferrous sulfide at 700°C. The similar conclusion was obtained from the relationships between vacancy concentration and sulfur activity determined previously by several authors. (English)

High-Temperature Oxidation of Metals and alloys —Histrical Retrospect and Prospect in Future—

K. Nishida

Corrosion Engineering (Boshoku Gijutsu)
23, 507 (1974)

This review paper describes the histrical progress in dry corrosion phenomena and the situation in future. That is, the theoretical development of dry corrosion begins with the studies of Pilling and Bedworth and Tammann on the thick scale formed on metals in the nineteen-twenties. C. Wagner showed firstly the parabolic oxidation theory by considering that corrosion was carried out by the movement of the charged particles through the scale and then many other researchers developed the theories to more complex systems. It contains many items like that: (1) General characteristics of high-temperature oxidation. (2) Classification of corrosion behaviors of metals and alloys. (3) Fundamental way of thinking about oxidation of alloys. (4) Mechanical properties of oxides and their relations to oxidation. (5) Protection techniques in future. Metals and alloys are impossible to protect themselves from the oxidation reactions at high temperature, so that they should be organically combined with ceramics as a protective scale. Therefore, it was finally emphasized that the combination processes of metals with such artificial ceramics would be an important problem in future. (Japanese)

Effects of Impurities and Specimen History on Bilayered NiO Scales

T. Ueno

Japan. J. Appl. Phys. **13,** 725 (1974), No. 4.

Nickel specimens with three different degrees of purity were heated in air at 1,170°C. Impurites contained in nickel enhanced the growth rates of oxide scales and made it easy to form the bilayered structure. Using the JEO micro-analyzer JXA–3, it was found that the metallic impurities started at a low level, rising increasingly with distance from the oxide/metal interface. The annealing of nickel specimen in a 10^{-5} Torr vacuum also enhanced the growth rates of the individual layers in bilayer formed on high purity nickel for except the inner layer in the black/black bilayer. (English)

Stresses in Bi-Layered NiO Scales

T. Ueno

Trans. Japan Inst. Metals **15,** 167 (1974), No. 3.

Different types of bi-layered scales of NiO can be formed in air on both sides of a thin nickel specimen at temperatures from 900 to 1,200°C. When the black/green bi-layer is formed on one side and the black/black bi-layer on the other side, a flexure of the specimen (99.9% pure) is achieved during oxidation ; the former is convex side. When removed electrochemically from the substrate of nickel (99 and 99.9 % pure), the black/green bi-layer was elongated causing bending to the opposite side. On the contrary, the black/black bi-layer formed on the 99.9% pure nickel remained straight with a negligibly small elongation as compared with the black/green bi-layer. It is found that high compressive stresses occur in the green layer, and negligibly small stresses in the black/black bi-layer. Macroscopic elastic stresses in the green layer at room temperature are estimated to be the order of magnitude 10^9 dynes/cm^2. Stress gradient across the scale are roughly estimated. Discussions are given on the formation of bi-layered structures. (English)

Growth of Bilayered NiO Scales on Nickel

T. Ueno

Japan J. Appl. Phys. **13,** 773 (1974), No. 5.

Four types of bilayered scale of NiO are formed on nickel in air over the temperature range of 900°C to 1,200°C. 1) The growth rates of scales on impure nickel show a deviation from the parabolic law and are given experimentally by $x^{1.7}=k_i t$. 2) The growth rates of scales on high purity nickel depend on the bilayered structures: The black/green bilayer (type R$_2$) grows approximately according to the parabolic law, while the black/black bilayer (type T$_2$) according to the two-stage parabolic law. 3) Diffusion of nickel along grain boundary is important for the formation of the black/black bilayer type T. 4) According to the colour and the electrical resistivity, the green inner zone of the type R,$_1$ T$_1$ and R$_2$ scales consists of stoichiometric NiO, while the black zone in the four types of scales contains an excess of oxygen. 5) The formation of the green inner zone in the type R$_1$, T$_1$ and R$_2$ scales may be due to the *metal consumption zone,* where oxygen is supplied by diffusions through the lattice coupled with the cation diffusion in a complex way and diffusion through the grain boundaries of scale. (English)

On the Bilayered NiO Scales Formed on Nickel

T. Ueno

J. Vacuum Soc. Japan (Shinku)
17, 315 (1974), No. 9.

In a series of investigations the author has studied the formation of the bilayered NiO scales: (1) The metallographic and crystallographic structures of the bilayer. (2) Effects of the impurities and specimen history on the bilayered NiO scales. (3) Stresses caused in the bilayered NiO scales. (4) Growth rates and electrical properties of the bilayered NiO scales. In this report they are reviewed on the basis of the physical properties of NiO. (Japanese)

Study on Oxidation of Iron by the Mössbauer Spectroscopy

H. Ohashi, M. Koizumi and T. Morozumi

Bulletin of the Faculty of Engineering, Hokkaido
University, No. **72,** 145 (1974)

Iron foil of 9.3 μm in thickness was oxidized in an oxygen atmosphere of 680 Torr at temperatures between 300 and 600°C. The Mössbauer spectra of oxidized specimens were observed as a function of the duration of oxidation. At temperatures higher than 400°C, Fe_3O_4 and α-Fe_2O_3 were mainly identified as the oxidation products, but no change of the spectrum was observed by heating for 20 days at 300°C. As a result of analysis of the spectra, it was clarified that the oxidation occurred from Fe to α-Fe_2O_3 through an intermediate Fe_3O_4 as a typical succesesive reaction at 500 and 600°C. The parabolic rate law fairly well satisfies the oxidation from Fe to Fe_3O_4 at 400°C and that from Fe_3O_4 to α-Fe_2O_3 at 500°C. The temporary appearance of α-Fe_2O_3 peaks in the initial stage of oxidation at 400°C was explained by assuming two competitive diffusion processes of Fe^{2+} through the Fe_2O_3 phase and O^{2-} through the α-Fe_2O_3 phase. (Japanese)

Oxidation of Uranium Dioxide

H. Ohashi, E Noda and T. Morozumi

J. of Nuclear Science and Technology,
11, 445 (1974)

The oxidation of UO_2 was studied by thermogravimetry and X-ray diffraction. It was clarified that the thermal history covering the first stage of the oxidation from UO_2 to U_3O_7 significantly influenced the rate of the oxidation of the second stage from U_3O_7 to U_3O_8. The entire oxidation reaction proceeded in what to all appearances, was a single stage when the specimen temperature was raised rapidly, whereas at slower rates of heating up, two distinct stages of oxidation were observed, separated by an intermediate induction period. These findings suggest the existence of a close connection between the rate of formation of the U_3O_7 phase and the rate of the subsequent oxidation of this phase: A slow formation of U_3O_7 would tend to prolong the induction period preceding the second stage of the oxidation. A similar effect was observed also with annealing of the intermediate U_3O_7 at 200°C: The increase of annealing time prolonged the induction stage. The rate of the second stage oxidation was fairly well expressed by Johnson & Mehl's equation, $\log (1/(1-y))=(1/2.303)k^n t^n$. The time exponent n in this equation varied in the range of 1.0~2.5, and the rate constant k of $1.15\times10^{-4}\sim2.04\times10^{-1}\mathrm{min}^{-1}$, depending on the experimental conditions. (English)

The Forms of Electrodeposits from $AlCl_3$–NaCl Baths at Moderate Temperatures

The Electrodeposition of Aluminium from Aluminium Chloride Baths (Part 1)

K. Itoh, T. Ishikawa and R. Midorikawa

SUMITOMO LIGHT METAL TECHNICAL
REPORTS, **15,** 259 (1974), No. 4.

This investigation was undertaken to explore the possibilities of the industrial application of electrolysis of aluminium chloride baths in a moderate temperature range. Cathodic polarization characteristics and the forms of deposits in the nearly equimolar region of $AlCl_3$–NaCl baths were studied potentiostatically and coulombstatically. The results obtained are as follows: (1) A pre-wave appears in the cathodic polarization curves obtained in the baths containing more than 50 mole % $AlCl_3$ at 400°C–505°C. (2) In the case of aluminium cathode, dendritic deposits are mainly formed by the electrolysis in the potential range where the pre-wave appears, whereas powdery ones are formed exclusively by the electrolysis at less noble potentials. In any way, smooth deposits suitable for electrowinning or electroplating of aluminium are not obtained at 400°–505°C. (3) In the case of copper cathode, the smooth deposits are formed to some extent in the same temperature range; however, continued electrolysis results in the formation of irregular deposits. (4) At temperatures higher than 574°C, molten Al–Cu alloyes are formed directly in the case of copper cathode. (5) At temperatures from 610°C to the melting point of aluminium, aluminium chloride in the baths can not be maintained at concentrations higher than 50 mole %, and minute globules or dendrites or partially molten dendrites are formed in the case of aluminium or tungsten cathode. The smooth deposits are not formed. (6) It seems reasonable to assume that the dendrites, formed on aluminium cathode at 400°–505°C, result from primary deposition, where-

as the powders result secondarily from the reaction of primarily deposited sodium with aluminium-containing ions in the bath. (English)

Corrosion Behavior of Metals in Fused Salts —Similarity to Higher Oxidation and Passivity—

T. Ishikawa

Fused Salt (YŌYŪEN), **17,** 264 (1974), No. 3.

From usual gravimetric measurements for corrosion studies, a parabolic rate law can be obtained in the oxide formation on iron and nickel immersed in alkali nitrate fused salts at 350–470°C. Activation energies around 35 kcal/mol are calculated from the temperature dependence of parabolic rate constant in these fused salts. Similar values have been found in the case of high-temperature oxidation of iron in an low pressure oxygen atmosphere. On the other hand, the corrosion of iron in the fused salt containing alkali and alkali earth halide obeys a linear rate law and halide ion can be detected locally in the oxide films formed on the corroding surface. These phenomena are similar to pitting corrosion of passive metals. Besides this pitting behavior, the corrosion rates of iron and nickel in the nitrate fused salt are greatly increased when these metal are either cathodically or anodically polarized. Taking into consideration a remarkable dissolution of active and transpassive metals, the natural corrosion state in the fused salt could be regarded as a passive state. (Japanese)

Distribution of Phosphate Ions in the Porous Anodic Oxide Film Formed on Aluminium in Phosphoric Acid Solution

H. Takahashi and M. Nagayama

J. Chem. Soc. Japan (Nippon Kagaku Kaishi)
(1974) 453, No. 3.

A porous oxide film having parallel pores is produced when aluminium is anodized in such a solution as phosphoric acid and a thin compact oxide layer called the "barrier layer" exists at the bottoms of pores. The thickness of pore-wall δ, which is a half of the distance between the adjacent pores, is nearly the same as that of the barrier layer, δ_b. It has been known that a small amount of phosphate ion is included in the film as the result of coordination of these ions towards aluminium ions in the oxide. In this investigation, the distribution of phosphate ion across pore-wall ($\delta=1{,}000$ Å) was measured for a film formed at 100 V (vs. SCE) in 4% H_3PO_4 kept at 25°C, a technique of dissolving the film in 2 mol/l H_2SO_4 solution being utilized. The dissolution of the film proceeds at the surface of pore-wall in such a manner that pore widens evenly all through the depth of the pore, so that the distribution of phosphate ion was determined by measuring the time-variations of the amounts of phasphate and aluminium ions in solution during dissolution. The concentration of phosphate is nearly constant irrespective of the distance, x, inwards from the surface of pore-wall until $x=400$ Å, but increases gradually beyond this position, attains a maximum value at $x=550$ Å, and decreases nearly equal to zero at 900 Å. The average concentration of phosphate in the film was estimated to be about 0.14 mg–PO_4/mg–Al. The distribution of phosphate across the barrier layer was similar to that across the pore-wall, in view of the results of examination of the film by ESCA and electronmicroscopy. The mechanism of film growth explaining the phosphate distribution is described. (Japanese)

Electronmicroscopic Observation of Active Sites and Micro-Pits in the Passive Film of Stainless Steel

T. Shibata

Boshoku Gijutsu, **23,** 615 (1974)

Nielsen's technique of platinum decoration for anodic sites was applied to detect the active sites and micro-pits produced by chloride attack in the passive film of Type 304 stainless steel. The number of active sites and micro-pits was found to depend on the potential of the film formation. Active sites on the anodically activated surface are evenly distributed, their number being $1.5 \times 10^{10}\,cm^{-2}$. On the surface covered with the passive film, the heterogeneous distribution is observed of active sites and also micro-pits. In the passivation potential region below 0.50 volt (vs. SCE), ca. $2.5 \times 10^{9}\,cm^{-2}$ of sites including active sites and micro-pits is counted, while at 0.60 volt the number of sites decreases to $4.7 \times 10^{8}\,cm^{-2}$ and again increases with potential, reaching to $1.2 \times 10^{9}\,cm^{-2}$ at 0.90 volt. A correlation between the site density and the induction time for the growth to macro-pits is discussed. (Japanese)

Analysis of Passive Films on Stainless Steel by Means of ESCA

G. Okamoto, K. Tachibana, T. Shibata
and K. Hoshino

J. Japan Inst. Metals, **38**, 117 (1974)

X-ray photoelectron spectroscopy, XPS, or ESCA was used to analyse a passive film formed on 18–8 stainles ssteel. ESCA spectra obtained from the passive surface treated at various potentials in 1N H_2SO_4 have shown distinct peaks of oxygen (OK), carbon (CK), and chromium Cr_{II}, CrL_{III}). Peaks of iron (FeL_{II}, FeL_{III}) in the spectra also were observed clearly, but those of nickel (NiL_{III}, NiL_{III}) were weak. The ratio of the peak height of CrL_{III} to one of FeL_{III} demonstrates a substantial enrichment of chromium in the passive film compared with the mechanicaly polished surface. Nickel is found not to be enriched. Two kinds of passive films are found, their chromium ratios depending on the formation potential. One is formed in a more basic potential region than a critical potential of 0.40 V (vs. SCE), showing an increase of chromium ratio with increase in the potential. The other having a higher and nearly constant the ratio is produced in the more noble potential region than the critical potential. (Japanese)

An Ellipsometric Study of Anodic Passivation of Nickel in Borate Buffer Solution

N. Sato and K. Kudo

Electrochimica Acta, **91,** 461 (1974), No. 8.

Ellipsometric and electrochemical measurements of the anodic passivation and secondary passivation films on nickel in borate buffer solution at pH 8.42 were made. The reference bare surface, obtained by cathodic reduction of electopolished nickel, gives the optical constants $N_3=1.65-3.81\ i$ for nickel. In the passivity region, where a little dissolution of nickel occurs, the surface film has the optical constants $N_2=2.7-0.25\ i$ and the film thickness as estimated by ellipsometry increases linearly with rise of the potential, from 4 to 13 Å, which is in fairly good agreement with the coulometrically estimated film thickness. In the oxygen evolution region, secondary passivation occurs with an abrupt increase in both optical constants and thickness of the surface film. The anodic passivation of nickel is compared with that of iron in terms of thickness of the surface film as a function of potential. (English)

Thickness and Structure of Passive Films on Iron in Acidic and Basic Solution

N. Sato, T. Noda and K. Kudo

Electrochimica Acta, **19**, 471 (1974), No. 8.

This paper describes the effect of solution pH on the passive film on iron which was investigated by ellipsometry and by cathodic reduction combined with chemical analysis. Anodic two-step passivation was employed to exclude anodic deposition of ferrous ion resulting from anodic oxidation of iron. The film in acid solution is almost anhydrous oxide, whereas the film in neutral and alkaline solution has an outer hydrated oxide layer, whose thickness decreases with decreasing pH. The hydrated outer layer depends also on the anion present in solution. The transition layer model of the film is proposed to explain the results. (English)

Anodic Passivation Films on Iron

N. Sato

Corrosion Engineering (Boshoku Gijutsu),
23, 535 (1974), No. 11.

Recent work on the structure and composition of the anodic oxide film on iron is reviewed. Experiments employing ellipsometry and cathodic reduction techniques show that the passive oxide film formed in neutral solutions is composed of two different layers, an inner layer adjoining to the metal and an outer layer in contact with the solution. Ellipsometric analysis indicates that the refractive index is 3.0–0.5 *i* for the inner layer and 1.8–0.1 *i* for the outer layer. Chemical analysis conducted during cathodic reduction of the film reveals that there is no detectable amount of ferrous ion Fe (II) in the inner layer as well as in the outer layer. Thermogravimetric experiments show that the anodic oxide film contains some amount of water probably concentrated in the outer layer. It is also shown that the inner layer thickness increases linearly with the anodic potential, whereas the outer layer thickness is almost independent of the potential. A practical model of the film is proposed in which the inner layer is a ferric oxide, probably γ-Fe_2O_3, containing a very little amount of water and the outer layer is a ferric hydroxide. The solution environment has direct effects on the outer layer which disappears in acidic solution, but has almost no effect on the inner layer which depends only on the overpotential of anodic oxide formation. (Japanese)

Ionic Current in the Passive Oxide Film on Iron

T. Noda and N. Sato

J. of the Japan Inst. of Metal,
38, 1143 (1974), No. 12.

The anodic passivity-maintaining current of iron in acidic sodium phosphate solutions of pH ranging from pH 1 to 6 has been investigated as a function of electric field in the passive film. The passive oxide film in acid solutions consists of a γ-Fe_2O_3 layer with an outermost hydrous oxide layer of negligible thickness and the overpotential produces a high electric field in the γ-Fe_2O_3 layer. At the steady state, the ionic current through the film, which is represented by the passivity-maintaining current, is equivalent to the dissolution rate of the film. It is shown that the ionic current depends on the electric field strength obeying the field-assisted ion migration mechanism. The self-diffusion coefficient and the apparent activation energy of ion migration are estimated for iron (III) and oxygen (II) ions, and compared with the diffusion data in the literature. It is suggested to be the oxygen ion that migrates in the film with the self-diffusion coefficient of 4.6×10^{-26} cm^2 sec^{-1} at 25°C and the activation energy of 11 Kcal/mol. (Japanese)

Chloride-Pitting Dissolution of Rotating Stainless Steel Electrode in Acid Solution

N. Sato, T. Nakagawa, K. Kudo
and M. Sakashita

Memoirs of the Faculty of Engineering, Hokkaido
Univ., Vol. XIII., Supplement, May, 163 (1972)

Anodic pitting dissolution, pit generation and pit growth of stainless steel at constant potential in sulphuric acid solution containing chloride ion have been investigated by use of rotating electrode. The electrode rotation makes the generation and growth of pits very stable and enables the pit generation frequency and the pitting current from a single pit to be measured potentionstatically. The pits break out at constant frequency and the rate of pit generation is a linear function of the potential, suggesting that the pit generation proceeds electromechanically rather than electrochemically. An incubation time, probably associated with the initial adsorption of chloride ion, is found before the linear pit generation commences, which differs from the induction time for opening an initial pit. The pitting current is in proportion to the area of pit mouth with the current density (8 A/cm^2) which is independent of the potential, indicating that mass transfer is rate-limiting. The pit grows following a parabolic law and the rate constant is an exponential function of the potential, from which a pit model is proposed in which the transpassive film continuously forming and breaking down on the inner pit surface assumes a high electric field. (English)

Testing Method and Reaction Mechanism on Corrosion under Heat-transfer Condition

T. Ishikawa and R. Midorikawa

Corrosion Engineering (Boshoku Gijutsu)
23, 183 (1974), No. 4.

A suitable equipment in which heat flux imposed perpendicularly to corroding surfaces was devised for corrosion test under heat transfer condition. A method for analysing experimental results was proposed in order to exclude effect of surface temperature and to evaluate heat transfer effect on corrosion rate. Using this equipment and according to this method, temperature changes and heat transfer effects on the corrosion rate of pure iron were investigated in nitrogen saturated acidic solutions. When the heat flux was in the same or the reverse direction as the metallic ion transfer in chloride and sulfate solutions, the corrosion rate increased or decreased at the same surface temperature. On the other hand, these heat transfer effects were negligible small in nitrate solutions. However, similar effect to that in the solutions of other anions was observed in the nitrate solution containing thiourea as a corrosion inhibitor. According to these experimental facts, a possible mechanism could be proposed. Changing the active sites on the surface, the heat transfer process affects indirectly to the rate of corrosion reaction. When the corrosion reaction is controlled by charge transfer process on the surface which is contaminated with adsorptive anions such as chloride and sulfate ions or with corrosion inhibitor such as thiourea, the corrosion rates in these solutions are affected by heat transfer process. On the other hand, presence of heat transfer does not affect the corrosion rate in the nitrate solutions in which the reaction rate is determined by hydrogen ion diffusion to the corroding surface, most of which is occupied by active sites. (Japanese)

Estimation of the Corrosion Rate of Steels in Neutral Solutions by the Measurement of Polarization Resistance

M. Nagayama, K. Goto, Y. Otake
and Y. Kawazu

Corrosion Engineering (Boshoku Gijutsu)
23, 57 (1974), No. 2.

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 device was developed to obtain the relationship between the anodic polarization and 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)

Estimation of Corrosion Rate of Metals by the Measurement of Electrochemical Polarization

M. Nagayama

J. Electrochem. Soc. Japan (Denki Kagaku)
42, 382 (1974), No. 8.

This review paper describes the basic principle of interpreting the polarization curves of metals and the methods of polarization measurement that have been adopted for the estimation of corrosion rate of metals in various environments. It was especially demonstrated that the polarization measurement is always accompanied by the change of sulface structure of metals which in turn is reflected by the change of polarizated potential with time. Significance of a 'rapid method' of polarization measurement and a 'polarization resistance method' was discussed in detail as methods of minimizing difficulty of the surface change. (Japanese)

Anodic Behavior of Strained Stainless Steels in Magnesium Chloride Solution

T. Shibata and T. Takeyama

J. Japan Inst. Metals, **38,** 124 (1974)

Anodic behavior of SUS 304 austenitic stainless steel in 0.5 M $MgCl_2$ has been studied at 25°C by means of a high speed elongation technique, in order to clarify the electrochemical condition for stress corrosion carcking of the steel. Anodic current of the steel increases by the elongation due to a newly created surface. High maximum current density (i_{max}) and rapid decay are observed at a constant potential in both of the active potential region and the passive potential region. i_{max} increases with potential between -0.5 V (vs. SCE) and 0 V, but, above 0V, no dependence is observed. Activation energy of i_{max} is found to be 5.54 kcal/mol. It is concluded that the anodic reaction showing i_{max} at the initial moment is controlled by the diffusion through the solution layer adjacent to the exposed surface. Analysis of current decay indicates that the logarithmic type of the film growth takes place below 0 V, and the parabolic type of the growth occurs at the more noble potential than 0 V, corresponding to the change of the potential dependence of i_{max}. The parabolic type of film growth has a close relation to pitting. Based on the potential dependence of i_{max} and the change in kinetics of the film growth, the electrochemical condition for stress corrosion cracking is discussed. (Japanese)

Dissolution and Film Formation of Fe–Cr–Ni Alloys in Boiling Magnesium Chloride Solution in Relation to Stress Corrosion Cracking

T. Shibata and T. Takeyama

Boshoku Gijutsu, **23,** 379 (1974)

High speed straining electrode technique has been applied for measuring the current for dissolution and film formation at newly created surfaces of iron, nickel, and several kinds of Fe–Cr–Ni alloys in bolling 46% $MgCl_2$ solution. Nickel content of alloys changes keeping chromium content between 15% to 19%. It is found that the maximum current density observed upon straining for a given amount at the corrosion potential decreases with the increase of nickel content. The film formation kinetics is described as $i=k/(Q-Q_0)^m$, where i is the current density, Q is the amount of charge involved and Q_0, k and m are constants. The value, m, also decreases with the increase of nickel content, exhibiting the highest value for 304 type steel. The higher susceptibility of alloys to stress corrosion cracking is closely connected with the higher maximum current density corresponding to the higher dissolution rate at fresh surfaces and also the larger value of m which indicates the higher inhibitive action of film against successive dissolution. (English)

Elementary Steps of Hydrogen Evolution Reaction at a Gold Electrode in Aqueous Sulfuric Acid

T. Sasaki and A. Matsuda

Chem. Lett., 141 (1974)

The rate and overvoltage of the constituent elementary steps of the hydrogen evolution reaction at a gold electrode in aqueous sulfuric acid were determined by means of a galvanostatic transient method together with a convenitonal steady state polarization method. It was concluded that the reaction proceeded through the discharge of hydrated proton which was followed by the recombination of adsorbed hydrogen atoms and the overvoltage of the former step was caused by the free charge on the electrode surface and that of the latter was attributed to the decrease in the electronic work function caused by the adsorbed hydrogen atoms. (English)

Exchange Rate of Electron Transfer Step of Hydrogen Evolution Reaction on Gold

T. Sasaki and A. Matsuda

J. Res. Inst. Catalysis, Hokkaido Univ.,
21, 157 (1974)

The exchange rate of the electron transfer step of the hydrogen evolution reaction on gold was determined separately from other steps in aqueous sulfuric acid and sodium hydroxide solutions by means of a galvanostatic transient method. The logarithm of exchange rate of electron transfer step changes linearly with pH of the sulfuric acid solution with a gradient 0.6 ± 0.15. This suggests that the electron transfer step in this solution consists of the discharge of hydronium ion. In alkaline solution the logarithm of exchange rate of electron transfer step changes linearly with the logarithm of the concentraction of Na^+ with a gradient of 0.5 ± 0.1 independent of pH of the solution. It may be concluded from this fact that the electron transfer step proceeds through the discharge of sodium ion as in the case of platinum and nickel. It is showed that the exchange rate of the discharge of hydronium ion is faster than that of sodium ion by about an order of magnitude. From the comparison the exchange rate of electron transfer step and that of the overall reaction, the former step, in any case, is not rate-determining at the reversible potential in sulfuric acid or aqueous sodium hydroxide. (English)

Dissolution of Zirconium in Aqueous Solutions of Ammonium Fluoride and Hydrofluoric Acid

T. Morozumi, M. Moriya and T. Kubo

Bulletin of the Faculty of Engineering, Hokkaido
University, No. **72,** 133 (1974)

The dissolution rate and the corrosion potential of zirconium were measured in aqueous solutions of ammonium fluoride and hydrofluoric acid at 30°C. The dissolution was rapid and uniform in both solutions, and the rate increased remarkably with the increase in concentrations of the solutions. In the case of ammonium flouride solution, the pH of the solution also showed an influence on the dissolution rate. The dissolution rate may be closely connected with the concentration of hydrogen fluoride existing in the form of neutral molecules in the solutions. In a thermodynamical sense, the depassivation by fluorides may be attributed to the formation of soluble fluoro-zirconium complexes. However, in order to explain the highly aggresive attack of fluorides on zirconium, certain dissolution mechanisms, in which the molecular HF or other fluoro-compounds can take a share of their contribution, must be assumed. (Japanese)

Electrodeposition of Copper from Cupric Pyrophosphate Solutions

H. Konno, K. Goto and M. Nagayama

J. Chem. Soc. Japan (Nippon Kagaku Kaishi)
(1974) 226, No. 2.

Cathodic current-potential curves were obtained for copper in cupric pyrophosphate solutions by using a rotating disk electrode, where the effect of concentration polarizations was completely eliminated. For all solutions tested, Tafel relations having a slope b of about -0.5 V were observed in the potential region of $-0.75\sim-1.0$ V (vs. SCE). The exchange current densitiy i_0 for the copper deposition reaction was obtained by extrapolating the Tafel line to the equilibrium potential of the reaction. It was found that i_0 increases with increasing concentration of $Cu(P_2O_7)_2^{6-}$ ion but decreases with the increase of $P_2O_7^{4-}$ ion concentration. From the results of experiments, the following mechanism was proposed in which $CuP_2O_7^{2-}$, produced by the dissociation of $Cu(P_2O_7)_2^{6-}$, is directly taking part in the electrode reaction.

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

$$CuP_2O_7^{2-} + 2e \longrightarrow Cu^0 + P_2O_7^{4-}$$

Semibright deposits were always obtained when the potential is more positive than -0.75 V as for as current is larger than about i_1 of 5 mA/cm. The value of the current i_2 at the critical potential of -0.75 V increases with increasing concentration of $P_2O_7^{4-}$. In the range of $i_1\sim i_2$, electrode surface is considered to be weakly adsorbed by pyrophosphate ions which enable random or smooth deposition of metal atoms. (Japanese)

Cathodic Polarization Characteristics of Iron in Chromic Acid Solutions Containing Sulfates

M. Izumiya and M. Nagayama

J. Metal Finishing Soc. Japan, **25,** 118 1974, No. 3.

Cathodic current-potential curves were measured for 99.4% iron in chromic acid solutions containing various amounts of sulfates. The curves were characterized by the presence of two current waves appearing respectively in the range of 0.40–0.95 V and below −0.95 V (vs. SCE). The partial currents for electrode reactions and the amounts of Cr and Fe ions incorporated into the chromic-chromate films were measured as a function of the cathode potential. The effect of solution composition was also examined. It was found that reactions $Cr(VI) \rightarrow Cr(III)_{aq.}$, $H^+ \rightarrow H_2$, and $Cr(VI) \rightarrow Cr(0)$ proceeded in parallel, but the deposition of metallic chromium was observed only in the potential region below −0.8 V. The chromium content or the thickness of chromium-chromate film was found to increase in a stepwise fashion with the lowering of potential. At any cathode potential, the thickness of the film decreased with the increase of sulfate concentration but the concentration of chromc acid had little effects on the film thickness. The Fe ion content of the film was considerably high above −0.45 V, but decreased to a small value when the potential was lowered to below −0.7 V. The characteristic feature of the current-potential curves and the mechanism of cathodic reduction of chromic acid were discussed in detail. (Japanese)

Formation of the Pyramidal Etch Hills on Pyrite and its Role in the Dissolution Kinetics

T. Nagai and H. Kiuchi

Journal of the Mining and Metallurgical
Institute of Japan, **90,** 653 (1984)

Optical, electron and scanning electron microscopies were used to study the pressure leaching of pyrite in $1\,N$–H_2SO_4. Natural pyrite single crystals from several mines with different grades of imperfections and synthetic pyrite single crystals were used as specimens. The optical microscopy showed that the high quality natural crystals dissolved uniformly, while the other crystals dissolved with some local corrosion which depends on their imperfections in the crystals. However, the electron microscopy revealed that pyramidal etch hills covered the whole surface of any specimen after the pressure leaching. The pyramidal etch hills were composed of $\{111\}$ planes regardless of the Miller indices of the surface. The sulphur droplets liberated by the reaction seem to inhibit the dissolution process at the points where they contact to the specimen, and hence they cause the development of the etch hills. The role of the formation of the pyramidal etch hills in the dissolution kinetics of pyrite was discussed. (Japanese)

Structural Change during Aging and Roasting of Hydrous Ferric Oxide and its Effect on the Adsorption Rate of CO–O_2 Mixture.

R. Furuichi, N. Sato and G. Okamoto

Memoirs of the Faculty of Engineering, Hokkaido
Univ., Vol. **XIII,** No. 4 (No. 61), 315 (1974)

The structural change that occurs during the aging and roasting of hydrous ferric oxide colloid was examined by measn of *X*-ray, DTA, and TGA. The initially amorphous oxide crystallized into α-Fe_2O_3 by aging and by roasting above 300°C, and doping Cu^{2+} retarded the crystallization of the aging process. The oxide contained three kinds of water, namely, adsorption water, bound water, and crystallization water, and the amount of bound water decreased by extending the aging time and hence by increasing the crystallinity. The effect of this structure change on the reactivity of oxide was studied by examining the consective adsorptions of CO–O_2 (mixing ratio$=2:1$ in volume) and/or CO at 30°C and 100°C. The adsorption kinetics at a constant pressure was found to be of a parabolic type ($V=k_d t^{1/2}$) for 30°C except for the initial period in which Wicke's equation was applied, and to obey Elovich's type $dV/dt=k\ \exp(-\alpha V)$ for 100°C. The adsorbed species of 30°C-adsorption was removed completely by outgassing at 100°C, and the species of 100°C-adsorption resulted in the change of the rate parameters (k and α) for the subsequent series of adsorption. These results were discussed with the assumptions that the amorphous oxide provided labile adsorption sites and the amount of bound water represented the amorphous part of the oxide. (English)

Effect of Surface Preparation on the Surface Composition of Fe–Ni Alloys

Y. Ohtake, K. Kudo and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
23, 135 (1874), No. 3.

An investigation has been carried out of the surface preparation of Fe–Ni alloys for corrosion and passivity study which often requires the alloy surface having practically the same composition as that of substrate alloy. Ellipsometric measurements of a 50 Fe–50 Ni alloy show that the surface prepared by electropolishing is optically different from the one prepared by mechanical polishing. ESCA spectroscopic measurements reveal that the electropolished surface layer of 50 Fe–50 Ni alloy contains no nickel, whereas both nickel and iron are present in the mechanically polished surface layer. Depletion of nickel at the electropolished alloy surface is also shown by anodic passivation and cathodic reduction of the surface. Air-formed oxide films on mechanically polished Fe–Ni alloys can be removed by cathodic reduction in a borate buffer solution of pH 6.45. The optimum current density and time for the cathodic reduction are given for various alloy composition. Mechanical polishing followed by cathodic reduction seems to be preferable to electropolishing followed by cathodic reduction for the alloy surface preparation in passivity study. (Japanese)

Work Function of Well-defined Surface of Copper-Nickel Alloy Plates

Y. Takasu, H. Konno and T. Yamashina

Surface Science **45,** 321 1974, No. 1.

The surface composition of copper-nickel alloy system was estimated by means of Auger electron spectroscopy and the work function was determined by monitoring the emission of photoelectrons from the well-defined surface. The value of the work function was highest in pure nickel and then decreased linearly as the copper content increased in the alloys. Thus, it is concluded that the work function of the copper-nickel alloy system is represented by the following equation: $\phi(X)=0.50X+4.43$, where $\phi(X)$ is the work function in eV, and X is the atomic fraction of nickel on the surface of alloys determined by Auger spectroscopy. (English)

Effects of Ion Bombardment on Adsorption and Exchange Reaction of Hydrogen by Evaporated Nickel Films

K. Watanabe and T. Yamashina

J. Catalysis **34**, 454 (1974), No. 3.

The effect of an activating treatment of evaporated films of nickel has been investigated by hydrogen adsorption and hydrogen-deuterium equilibration reaction in the pressure range 10^{-6}–10^{-3} Torr at room temperature. Adsorbed hydrogen can be divided into reversible and irreversible parts. The former can be removed easily by pumping at near room temperature, while the latter cannot. A Freundlich isotherm fits the reversible adsorption data while the irreversible adsorption is best described by a Langmuir isotherm (with dissociation). Argon ion bombardment gave drastic increase in hydrogen adsorption, although the surface area of the nickel film measured by xenon adsorption showed no change with either ion bombardment or annealing. The rate of equilibration was found to obey the rate law, $V=kP^{1.3}$ after either ion bombardment and annealing (the values of k were exactly the same on both the films). It is concluded that the rate of the equilibration is controlled by the reaction step, $2\,\mathrm{H}(\mathrm{a})_{\mathrm{irr}}+\mathrm{D}_2(\mathrm{a})_{\mathrm{rev}}=2\,\mathrm{HD}$, and that only a small part of the dissociative hydrogen which is irreversibly adsorbed appears effective in the equilibration reaction near room temperature. It is also concluded that on these particular sites, there are no effects of bombardment or annealing on the overall rate of the equilibration near room temperature. (English)

Crystal Structure of Reactive Sputtered Silver Films and Thermal Desorption of Oxygen from These Films

S. Tanaka, T. Abe and T. Yamashina

Chemistry Letters 599 (1974), No. 6.

The crystal sturucture and resistivity of silver films sputtered in an oxygen atmosphere and the thermal desorption of oxygen from these films were studied. The sputtered silver films prepared under the oxygen of 1.5×10^{-4} and 3×10^{-4} Torr contained very fine fcc silver crystals and Ag_2O crystals. The thermal desorption showed that all the reactive sputtered silver films contained a considerable amount of an amorphous phase. (English)

Constant Voltage Electropolishing for Iron and Nickel

N. Sato, K. Kudo and T. Noda Corrosion,
30, 237 (1974), No. 7.

This note describes a convenient and reliable procedure for electropolishing iron and nickel in Jacquet's solution for laboratory purposes. In a Jacquet's solution containing glacial acetic and perchloric acids, the anodic dissolution current of iron and nickel increased with the cell voltage (region I) until it was almost constant (region II). Further rise of the cell voltage resulted again in an increase of the dissolution current (region III). The surface of iron and nickel electropolished in the voltage region I, II and III was examined electron-microscopically and it was shown that the optimum voltage for polishing was in the voltage region II. Since the anodic current slightly depends on the cell voltage in the region II, constant-voltage electropolishing is more advantageous than constant-current polishing. The recommended procedure is as follows ; (1) Use Jacquet's solution at 15 C under a fixed agitation condition, (2) measure the current-voltage curve, (3) determine the optimum voltage at a value slightly smaller than the voltage at which transition of the diffusion-limited current to the oxygen evolution occurs, and (4) perform the polishing in 10 second bursts by controlling the cell voltage at this optimum value. (English)

Spectrophotometric Determination of Aluminium with Ferron and a Quaternary Ammonium Salt

K. Goto, H. Tamura, M. Onodera and M. Nagayama

Talanta, **21,** 183 (1974), No. 3.

The reproducibility of the ferron method for analyzing aluminium has been greatly improved by the addition of cetyltrimethylammonium chloride (CTMAC). The improvement is attributed to reduction of the reagent blank and increased stabilityof $Al(ferron)_3^{3-}$. The alumininm-ferron complex formed in the presence of CTMAC has an absorption peak at 385 nm. The interference from iron can be eliminated by application of a correction based on measurement at two wavelengths. The recommended procedure is as follows: Place an aliquot of sample containing not more than 60 μg of aluminium in a 25-ml volumetric flask, add 2 ml of ferron solution (0.8%), 3 ml of acetate buffer (pH 5) and 5 ml of CTMAC–KCl solution (2%–1.5%). Dilute to volume and measure the absorbance at 385 nm against a reagent blank. (English)

Spectrophotometric Determination of Iron (II) with 1, 10-Phenanthroline in the Presence of Large Amounts of Iron (III)

H. Tamura, K. Goto, T. Yotsuyanagi
and M. Nagayama

Talanta, **21,** 314 (1974), No. 4.

A study was made to establish proper conditions for the selective determination of Fe(II) by the 1, 10-phenanthroline method in the presence of large amounts of Fe(III). It was shown that Fe(III) is effectively masked by fluoride. The pH of the solution to be masked should be below 2.5 in order to prevent acceleration by the fluoride of aerial oxidation of Fe(II). The recommended procedure is as follows: Pipette 15 m*l* of sample solution containing Fe(II) (up to 7 ppm) and Fe(III) (up to 2,500 ppm) into a polyethylene beaker. Add 1 m*l* of sulphuric acid (1+4), 2 m*l* of ammonium fluoride solution (2 M), 2 m*l* of 1, 10-phenanthroline solution (1%), and 3 m*l* of hexamethylenetetramine buffer (3 M) in that order, swirling the solution after addition of each reagent. Transfer the solution to a 25-m*l* graduated flask and dilute to the mark. Mix thoroughly and measure the absorbance at 510 nm. (English)

Quantitative Measurement of Mass Spectra with Quadrupole Mass Filter-Sputter Ion Pump System

M. Hashiba, T. Hanasaka and T. Yamashina

J. Vacuum Soc. Japan **17,** 186 (1974), No. 6.

Reproducibility and stability in pattern coefficient of a quadrupole mass filter in a sputter ion pump system have been studied systematically. In order to the quantitative measurement of dynamic re-emitted gases from the ion pump, a conductanice adjusting valve was inserted between the measuring chamber and ion pump. Before admission of gases, most of residual gases such as hydrogen, nitrogen and some hydrocarbons were observed not to increase with increase of total pressure by closing the adjusting valve, while argon and methane were increased. When propylene was admitted into the chamber as sample gas, the minimization of the re-emission of gases was achieved in case of 5–10 as the pressure ratio between the chamber and pump in this study. Although the re-emission from the pump reduced for larger pressure ratio, the dynamic re-emission from the cahmber increased considerably as closing the valve, in spite of the relatively small amount of residual gases as seen in the case before gas admission. Comparison of the reproducibility in pattern coefficient of the mass filter with and without electron multiplier was also investigated systematically. The fluctuation coefficient $2\sigma/\bar{x}$ (σ : standard deviation, $\bar{x}$: mean value of pattern coefficient) was approximately 2 percent and no troublesome effect by the multiplier was found in the quantitative analysis within the period of three days. (Japanese)

Electrochemical Polarization Characteristics and Ion Transport through Ion Exchange Membranes in Sodium Chloride Solution

M. Sakashita and N. Sato.

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The polarization behavior and transport property of cation and anion exchange membranes (CMV, AMV) in dilluted NaCl aqueous solutions were investigated by potentiostatic and galvanostatic techniques, and the application of these membranes to desalination was discussed. Both potentiostatic and galvanostatic I–V curves gave the same limiting current densities, which were coincident with the current densities at which the pH values of bulk solution began to increase or decrease in galvanostatic pH–I curves. The diffusion constants of Cl^- and NaCl through CMV were determined by using radioisotope ^{36}Cl to be $\bar{D}_{Cl}=5\times10^{-8}\,cm^2\cdot sec^{-1}$and $\bar{D}_{NaCl}<10^{-9}\,cm^2\cdot sec^{1-}$. The transport number of Na^+, Cl^- and H^+ ions for CMV were estimated by measuring the flow of ^{36}Cl and the increase of solution pH. Furthermore, the concentration difference between the two interfacial solutions of both sides of CMV was calculated from the Cl^- transport through the membrane. (English)

Disposal of Waste Chemicals

M. Nagayama and K. Goto

J. Chem. Education of Japan (Kagaku Kyoiku),
22, 407 (1974, No. 5.)

Basic principles for the treatment of poisonous ions such as CN, As, F, Cr, Pb, Cd, Zn, Hg, Cu, Ag, which are found in waste solutions from laboratories are discussed and the process designed for the plant established at the Hokkaido University is explained in detail. The process can be applied to the waste water treatment in metal finishing industries. (Japanese)