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ELECTROMETALLURGY LABORATORY

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

Students

M. Okazaki, H. Tanaka, Y. Shinno, T. Iwata,
H. Shimizu, S. Suzuki, K. Nakayama
and K. Nishimura

Research subjects in progress are as follows.

(1) Laboratory scale tests in bipolar electrode cells for electrowinning of liquid aluminum are being carried out by using alkali and alkaline earth chlorides molten salts containing aluminum chloride in the temperature range from 700° to 800°C.

(2) The rotating bipolar electrode stack cell for recovery of heavy metals is being tested under various electrolytic conditions in dilute cupric sulfate solutions, and its fundamental functions are also being investigated using the single electrode cell composed of a rotor electrode and a stator electrode.

(3) Inhibition mechanisms of organic corrosion inhibitors for metals and alloys are being studied using electrochemical techniques.

(4) In order to elucidate the effect of small gas bubbles in tap water on the corrosion of pipe-line materials, loop-tests of corrosion are carried out under controlled conditions.

Oral Presentation

Effect of Rotation and Flow Rate on the Diffusion Limiting Current in Rotating Bipolar Electrode Stack Cell; T. Sasaki and T. Ishikawa: The 9th Hokkaido Section Meeting of Electrochem. Soc. of Japan, Jan., 1983.

Electrowinning of Liquid Aluminum by using Bipolar Electrode Cell —On the Operation of Rectangular Cell—; M. Okazaki, S. Konda and T. Ishikawa: *ibid.*, Jan., 1983.

On the Inhibition of Dezincification of Brasses by Corrosion Inhibitors ; T. Notoya and T. Ishikawa : The 18th Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1983.

Effect of Flow Rate and Gas Bubbles on the Corrosion of Steel Pipe-line ; S. Ohta and T. Ishikawa : *ibid.*, Jan., 1983.

Dezincification Prevention of Copper Alloys using Corrosion Inhibitors ; T. Notoya and T. Ishikawa : The 1983 Winter Meeting of the Hokkaido Section of the Japan Chemical Society, Feb., 1983.

Introduction to Corrosion Protection of Metals ; T. Ishikawa : 1983 Short

Electrochemical Treatment of Cupric Sulfate Solution with Rotating Bipolar Electrode Stack Cell (Part 4) Effect of Surface Properties on Copper Deposition ; U. Shinno, T. Sasaki and T. Ishikawa : The 50th Annual Meeting of the Electrochem. Soc., Japan, March, 1983.

Development of Aluminum Electrowinning Process with Chloride Melt and Bipolar Electrode Cell (Part 2) Heat Transfer Characteristics of Particles-Packed Cell Wall ; T. Ishikawa, S. Konda and A. Kumatoritani : *ibid.*, March, 1983.

Inhibition Effect of Some Inhibitors on Dezincification Corrosion of 60/40 Brass in Chloride Solutions ; T. Notoya and T. Ishikawa : The Spring Meeting of the Japan Institute of Metals, April, 1983.

Evaluation of Bipolar Electrode Cell for Electrowinning of Liquid Aluminum from Chloride Melts ; T. Ishikawa and S. konda : First International Symposium on Molten Salt Chemistry and Technology, (Kyoto), April, 1983.

Inhibition Action of Organic Inhibitors against 60/40 Brass Dezincification in NaCl Solution ; T. Notoya and T. Ishikawa : '83 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1983.

On the Prevention of Dezincification Attack in Brasses by Heterocyclic Organic Compounds ; T. Notoya and T. Ishikawa : The Spring Meeting of Hokkaido Section of Japan Institute of Metals, June, 1983.

Simple Network Model of Bipolar Electrode; T. Sasaki and T. Ishikawa: '83 Hokkaido Section Summer Meeting of Japan Chem. Soc., July, 1983.

Corrosion of Steels under Heat Transfer Conditions; T. Ishikawa: Seminar of the Corrosion Metals sponsored by the Hokkaido Corrosion Research Association, Aug., 1983.

Effects of Organic Compounds on Growth of Dezincification Layer in Brasses; T. Notoya and T. Ishikawa: The 48th Fall Meeting of Japan Chemical Society, Aug., 1983.

Dezincification Behaviours of 70/30 Brass in Chloride Solutions with Organic Inhibitors; T. Notoya and T. Ishikawa: The Fall Meeting of Japan Institute of Metals, Oct., 1983.

Protection of Brasses from Dezincification Attack by Organic Inhibitors; T. Notoya: The 32rd Meeting of Japan Copper and Brass Research Association, Nov., 1983.

Effect of Accumulation of Deposited Metal on Electrolytic Rate of Dilute Cupric Sulfate Solution; T. Sasaki and T. Ishikawa: The 1983 Fall Meeting of the Electrochem. Soc. of Japan, Nov., 1983.

Decomposition Voltage of Aluminum Chloride in the High-temperature Chloride Melts; H. Tanaka, S. Konda and T. Ishikawa: *ibid.*, Nov., 1983.

Development of Aluminum Electrowinning Process with Chloride Melt and Bipolar Electrode Cell (Part 3) On the Structure of Cell Wall; T. Ishikawa and S. Konda: *ibid.*, Nov., 1983.

Development of Aluminum Electrowinning Process with Chloride Melt and Bipolar Electrode Cell (Part 4) Construction and Operation of Internal-heating Simulation Cell; S. Konda and T. Ishikawa: *ibid.*, Nov., 1983.

Application of Corrosion Inhibitors to Prevention of Dezincification Attack in Brases; T. Notoya: The 2nd Meeting of Copper Alloys Corrosion Research Group, Dec., 1983.

ELECTROCHEMISTRY LABORATORY

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

Students

K. Azumi, T. Shimakura, F. Baba, N. Goto,
Y. Kameya and N. Nakaya

Research Fellow

Y. Kawamura

Current research in this laboratory may be divided into five groups : a) theoretical approaches to metallic corrosion and passivation from thermodynamic and kinetic viewpoints, b) electron spectroscopic studies of surface layers of anodically or thermally oxidized metals and alloys, c) reflectometric and light-scattering studies of surface oxide films on metals, d) electrochemical studies on the ion-selective and electro-osmotic properties of corrosion precipitate films, and e) electrochemical studies of the electrode/solution interface.

Research subjects in progress are as follows

(1) Quantitative analysis of surface layers by AES and ion-sputter etching : Relationship between ion-sputter etching and depth profiling by AES is quantitatively treated and the spread of the interface region between oxide and metal substrate is analysed.

(2) Enrichment and depletion of alloying elements in surface layers of iron-base alloys oxidized in aqueous and gaseous environments : Enrichment or depletion of elements in the substrate alloy plays some roles for anti-corrosion properties of the alloys as well as its surface oxide.

(3) In-situ reflectometric studies of the passive films on iron, nickel and titanium : Spectra of complex refractive index of the passive films are measured as well as the thickness-potential relationship.

(4) Anodic oxidation of niobium in neutral solution: The film growth is being measured in neutral borate solutions containing NaCl.

(5) Surface stress detection by potential modulation: Surface stress of gold and platinum electrodes is being measured by using a piezo detector with a potential-modulation technique.

(6) Application of Raman scattering spectroscopy to corrosion research: Raman scattering spectroscopy is being applied to the study of surface films thermally formed on stainless steel and anodically formed on titanium.

(7) Development of a faced rotating-disc stationary-ring electrode (FRDSDE)

(8) Ionic flow, mass transport, and electro-osmosis related to crevice corrosion: The property of corrosion product is of importance to understand the crevice corrosion which is being analyzed by use of a model crevice from the ion-selectivity and electro-osmotic property of the corrosion precipitate.

Foreign visitors to this laboratory in 1982 are Prof. Dr. K. G. Weil from the Technishe Hochschule Darmstadt in FRG on April 6–9, Dr. S. R. Keown from Beta Metallographic Services in U. K. on July 7–8, Dr. R. Papaleo from CBMM Brazil on July 7–8, Dr. M. G. S. Ferreira from University Lisbon in Portugal from August 1 to October 15, Dr. K. K. Kuzemraevich from the Institute of Organic Catalysis and Electrochemistry in USSR on November 10, and Dr. R. S. Alwitt from the United Chemi-Con Inc. in USA on Nov. 17.

Oral Presentation

Anodic Film Composition and Oxidation Behaviour of Iron-Base Alloys in Concentrated Alkaline Solution; M. Seo, Y. Sera and N. Sato: The 9th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1982

Behaviour of Cathodic Reduction of Passivation Film on Iron by Rotating Pt Ring-Fe Disc Electrode; I. Shintani, T. Ohtsuka and N. Sato,: *ibid.*, Jan., 1982

Ionic Selectivity and Electro-Osmose of Precipitate Membrane Composed on Iron (III) Oxide ; M. Sakashita, T. Shimakura and N. Sato : The 18th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1982

Surface Characterization of Metallic Catalysts by AES ; M. Seo : The 16th Meeting for Coal Investigation in Hokkaido, Feb., 1982

Investigation of Surface Passivation Films on Iron in Aqueous Solution by Reflectivity of Polarized Light ; T. Ohtsuka, K. Azumi and N. Sato : The 2nd Discussion Meeting of the Japan Society of Surface Science, Feb., 1983

Mass Transport in Crevice Covered with Precipitate of Iron Oxide ; M. Sakashita : Special Meeting of the Japan Society of Corrosion Engineering on Crevice Corrosion, Feb., 1983

Estimation of Amount of Fe (II) Ion Cathodically Dissolved from Passivation Film on Fe by Rotating Ring-Disc Electrode ; T. Ohtsuka, I. Shintani and N. Sato : The 50th Annual Meeting of Electrochem. Soc. of Japan, March 1983

Two-Layer Structure of Passive Films on Iron by Reflectivity Measurement ; K. Azumi, T. Ohtsuka and N. Sato : '83 Meeting of the Japan society of Corrosion Engineering, May, 1983

Ionic Flow and Electro-Osmososis in Crevice of Stainless Steel Covered with Fe (III)-Oxide Precipitate ; M. Sakashita,, T. Shimakura and N. Sato : *ibid.*, May, 1983

Reflectometry of Iron Passivation Films in Neutral Borate and Acidic Phosphate Solutions ; T. Ohtsuka, K. Azumi and N. Sato : The 5th Intern. Symposium on Passivity (Bombannes-France), May, 1983

Optical and Impedance Studies of Nickel Passivation Film in Neutral Solution ; T. Ohtsuka, K. Azumi and N. Sato : *ibid.*, May, 1983

Mass Transport in Precipitate Memberane of Fe (III)-Oxyhydroxide and Crevice Corrosion ; T. Shimakura, M. Sakashita and N. Sato : The Spring Meeting of Hokkaido Section of JIM., May, 1983

An In-Situ Reflection-Spectroscopic Study Applied to Anodic Oxide Films on Fe, Ni. and Ti; T. Ohtsuka, K. Azumi and N. Sato: Intern. Conf. on Ellipsometry and Other Optical Methods for Surface and Thin Film Analysis (Paris-France), June, 1983

Anodic Oxidation Behaviour and Surface Film Composition of Nb in Acidic Auqeous Solution; M. Seo, K. Inanaga and N. Sato: The Summer Meeting of Hokkaido Section of the Japan Chemical Society, July, 1983

Anodic Oxide Film on Hg-Te in Aqueous Acetic Acid Solution; M. Sakashita and N. Sato: *ibid.*, July, 1983

Ellipsometry of Electrode-Solution Interface; T. Ohtsuka and N. Sato: The 48th Autumn Meeting of the Japan Chemical Society, Aug., 1983

Selective Surface Oxidation of Fe-Ni and Fe-Cr Alloys and Depth Profile in the Substrate Alloys; M. Seo and N. Sato: *ibid.*, Aug., 1983

Outstanding Achievement Award Lecture-Ion-Permeability of Corrosion Precipitate Films: N. Sato: The 1983 Fall Meeting of the Electrochem. Soc. (Washington-USA), Oct., 1983

Formation and Reduction of Anodic Oxides on Hg-Te and $Cd_{0.2}Hg_{0.8}Te$; H.-H. Strehblow, C. Calinski, B. P. Löchel and M. Sakashita: *ibid.*, Oct., 1983

Spread of Depth Profile at Oxide Film-Substrate Metal Interface due to Sputter Etching; M. Seo and N. Sato: The 93th Fall Meeting of JIM., Oct., 1983

Spectra of Passivation Film on Iron by Reflectivity Measurements; T. Ohtsuka, K. Azumi and N. Sato: The Discussion Meeting of the Japan Society of Corrosion Engineering, Nov., 1983

Quantitative Surface Analysis of Passive Films on Iron-Base Alloys; M. Seo: Seminar on Japan-Sweden Collaboration Research (Stockholm-Sweden), Nov., 1983

Depth-Profiling of Surface Oxide Film/Metal System; M. Seo and N. Sato: The 3rd Intern. Conf. on Quantitative Surface Analysis, (Teddington-U. K.), Nov., 1983

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

K. Ogura, N. Sato, K. Ito, M. Taniguchi, T. Sato,
T. Tabuchi and Y. Yasue

Prof. H. Ohashi returned from the work with Prof. Donald R. Olander at the University of California, Berkeley, U. S. A. Dr. T. Mizuno will go abroad next March to work with Prof. J. O' M. Bockris at Texas A & M University.

Our laboratory is mainly concerned with studies on corrosion of metallic materials used in nuclear industries, Mössbauer spectroscopic characterization of iron rust and improvement in the performance of hydrogen reservoir alloys.

Research subjects in progress are summarized as follows :

(1) Corrosion in molten FLINAK salt was investigated for various metal alloys, such as SUS 304, SUS 316, Inconel 600 and Hastelloy-B, -C, -C276, -N and -X. The investigation was especially on the effect of Mo and C on the corrosion behavior of these alloys.

(2) Corrosion of SUS 304 and 316 were electrochemically investigated in various decontamination reagents for primary water-coolant circuits of nuclear reactors.

(3) A method of measurement and analysis of transient electrode reactions is under development by using a micro-processor controlled device.

(4) Mössbauer spectroscopy and other characterization methods were used for an investigation of the controlling parameters and mechanisms in the formation processes of major components of iron rust, such as superparamagnetic α-FeOOH and α-Fe_2O_3, anti-

ferromagnetic α-FeOOH, α-Fe_2O_3 and γ-FeOOH, and also ferrimagnetic γ-Fe_2O_3.

(5) Characterization was carried out to clarify the pulverization process of nonstoichiometric Ti-Fe alloys as a function of hydrogenation and dehydrogenation cycles by Mössbauer spectroscopy, BET surface area measurement, and other methods. Zinc coating was proposed as an effective means for preventing the pulverization of these alloys.

Oral Presentation

Use of Scanning Transmission Electron Microscopy (STEM) for the Study of Anodic Films; M. Moriya: Symposium on Anodic Films, Hamilton, Canada, May 1981.

Passive Films on Nickel Alloys — Applications of AES, ESCA and STEM; M. Moriya, V. Scepanovic and M. B. Ives: Discussion Meeting on Surface Analysis and Surface Properties, Hamilton, Canada, March 1982.

Scanning Transmission Electron Microscopy of Anodic Films Formed on Nickel and Nickel-Molybdenum Alloy; M. Moriya and M. B. Ives: Chalk River Nuclear Laboratory, Chalk River, Canada, June 1982.

Scanning Transmission Electron Microscopy of Anodic Films Formed on Nickel and Nickel-Molybdenum Alloy; M. Moriya and M. B. Ives: National Research Council, Ottawa, Canada, June 1982.

Scanning Transmission Electron Microscopy of Anodic Films Formed on Nickel and Nickel-Molybdenum Alloy; M. Moriya and M. B. Ives: Whiteshell Nuclear Research Establishment, Pinawa, Canada, June 1982.

The Structure of Passive Films on Single Phase Nickel-Molybdenum Alloys; M. B. Ives, V. Scepanovic and M. Moriya: 5th International Symposium on Passivity, Bordeaux, France, May 1983.

Observation of Anodic Film of Nickel-Molybdenum Alloys by Scanning Electron Microscopy; M. Moriya and M. B. Ives: The

18th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1983.

Improvement of Durability of Fe-Ti Hydrogen Reservoir Alloy; T. Mizuno and T. Morozumi: The 1983 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb., 1983

Prevention of Pulverization of FeTi Hydrogen Reservoir Alloy with Coating of Low Melting Alloy; T. Mizuno and T. Morozumi: The Joint Spring Meeting of the Hokkaido Sections of Japan Institute of Metals and Iron and Steel Institute of Japan, June, 1983.

Changes in Properties and Structure of FeTi Hydrogen Reservoir Alloy by Hydrogenation and Dehydrogenation; T. Mizuno, N. Sato and T. Morozumi: The 1983 Summer Meeting of the Hokkaido Sections of the Japan Chemical Society and the Japan Society for Analytical Chemistry, July 1983.

Corrosion of Hastelloy-N in Molten Fluoride Salt; M. Moriya and T. Morozumi: *ibid.,* July 1983.

Application of Mössbauer Spectroscopy in the Study of Corrosion; H. Ohashi: National Research Council, Ottawa, Canada, Oct., 1983.

Measurements of High Temperature Oxidation Rates of Iron by Mössbauer Spectroscopy; H. Ohashi: Argonne National Laboratory, Argonne, U. S. A., Oct., 1983.

Measurements of High Temperature Oxidation Rates of Iron by Mössbauer Spectroscopy; H. Ohashi: Oak Ridge National Laboratory, Oak Ridge, U. S. A., Oct., 1983.

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

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

Students

G. Kanoh, N. Inaba, S. Kawamura, H. Odagiri,
Y. Murosawa and K. Katoh

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

(1) New development in the hydrogen production technology using H_2S and metal sulfides from metallurgical processes.

The two-step thermochemical cycle shown below is proposed for recovering hydrogen from H_2S and fundamental studies on this cyclic reaction is made.

$$\begin{array}{l} Ni_3S_2 + H_2S = 3NiS + H_2 \\ 3NiS = Ni_3S_2 + \frac{1}{2} S_2(g) \\ \hline H_2S = H_2 + \frac{1}{2} S_2(g) \end{array}$$

Based on the experimental results obtained above, use of the pellets consisting of finely dispersed nickel sulfide on kieselguhr and scale-up tests are examined. Furthermore, the Ni–Cr–S ternary sulfides are synthesized and thermochemical splitting of H_2S with these sulfides are also conducted.

(2) Pyrohydrolysis of metal chlorides and its application to the reduction of metal chlorides and sulfates.

Much ferrous chloride is obtained as a by-product in ferric and cupric chloride leaching of copper concentrates. Also, pyrohydrolysis of metal chlorides has recieved much attention not only in the metallurgical field but also in the energy field relevant to thermochemical decomposition of water. Reduction of metal chlorides or sulfates with hot gas from pyrohydrolysis of ferrous chloride and effect of HCl gas on the reduction of metal chlorides and sulfates are being examined.

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

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

Oral Presentation

A Fundamental Study on Hydrogen Recovery using the reaction between Molten Metal and Hydrogen Sulfide; Y. Nakai, H. Kiuchi and T. Tanaka: The 1983 Winter Meeting of the Hokkaido Sections of JSAC and JCS, Feb. 1983.

A Study on the recovery of Hydrogen from Hydrogen Sulfide with Nickel Sulfide; T. Tanaka and H. Kiuchi: The Meeting on Chemical Energy, Grant-in- Aid for Energy Research, The Ministry of Education, Science and Culture, Jan. 1983.

A Study on Effective Utilization of Hydrogen Sulfide (IX); H. Kiuchi, S. Tasai and T. Tanaka: The Annual Meeting Min. Met. Inst. Japan, Apr. 1983.

Hydrogen Pressure Reduction of Copper Electrolyte (III): R. Togashi and T. Nagai: *ibid.*, Apr. 1983.

Purification of Copper Electrolyte by Means of Solvent Extraction; G. Kanoh and T. Nagai: *ibid.*, Apr. 1983.

Purification of Copper Electrolyte by Means of Chelating Resin; G. Kanoh and T. Nagai: The Spring Meeting of the Hokkaido Section, Min. Met. Inst. Japan, June 1983.

Recovery of Hydrogen and Elemental Sulfur from Hydrogen Sulfide (VII): N. Inaba, H. Kiuchi, S. Tasai and T. Tanaka: *ibid.*, June 1983.

Approach to Hydrogen Production through Sulfide Smelting; T. Tanaka, H. Kiuchi, R Shibayama and S. Tasai: The 48th Annual Meeting of JCS, Aug. 1983.

Extractive Metallurgy and Hydrogen; T. Tanaka, H. Kiuchi and R. Shibayama: Celebration Meeting of the 10th Anniversary of the Hydrogen Energy Society of Japan, Sept. 1983.

Recovery of Hydrogen and Elemental Sulfur from Hydrogen Sulfide (VIII); N. Inaba, H. Kiuchi and T. Tanaka: The Autumn Meeting of the Hokkaido Section, Min. Met. Inst. Japan, Nov. 1983.

Purification of Copper Electrolyte by Means of Chelating Resin (II); G. Kanoh and T. Nagai: *ibid.*, Nov. 1983.

Purification of Electrolyte; T. Nagai: The 8th Symposium on Non-Ferrous Extractive Metallurgy, Nov. 1983.

Removal of Arsenic from Geothermal Hot-Water by Hydrated Zirconium Oxide; T. Nagai and R. Togashi: The Meeting on Natural Energy, Grant-in-Aid for Energy Research, The Ministry of Education, Science and Culture, Nov. 1983.

Removal of Antimony, Bismuth and Iron in Copper Electrolyte by a Chelating Resin; G. Kanoh and T. Nagai: The Symposium on Solvent Extraction 1983, Dec. 1983.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

K. Kegasawa, K. Watanabe, M. Masuda, T. Iizuka,
Y. Ishida, T. Sawada, H. Torii, W. Nakagawa
and K. Fujishima

Researches in progress are as follows :

(1) Strength tests by micro-size specimen were started on gray cast iron to clarify the role of graphite flakes. Tensile tests using specimen of diameter 2, 4, 8 and 12.5 mm were performed on FC 25 grade cast iron. No clear effect of specimen size on the tensile strength was obtained.

(2) Impact strength of S. G. iron with different graphite nodule size was tested by an instrumented charpy impact machine at temperatures lowered to the liquid nitrogen temperature. The transition temperature of fine graphite nodule iron was lower about 100°C than that of coarse graphite iron. The nodule size might affect the resistance to the initiation of rapid propagation of crack.

(3) Residual stress in gray iron castings was measured by the holedrilling method applicable to the industrial analysis. Effects of temperature of break out of moulds and the annealing on the stress were analyzed effectively.

(4) Medium carbon steel was heat-treated to get phases of ferrite and matensite, and paying attention on the martensite ratio the properties of steel were examined. Quenching strain might be lowered in the dual phase steel.

(5) Tests of surface-hardening of sintered iron by the self carburizing was continued to verify the phenomenon suggested

formerly. A successful quench-hardening was obtained in a specimen heated to 930°C for 30 min in the oxygen reduced air of 6% O_2. The hardness reached to 730 Hv at the surface with matrtensitic structure.

(6) Isothermal expansion of coarse flake cast iron at austenite temperature was examined in relation to the cyclical growth in the region, and the results were attributed unifiedly to the self carburizing.

Oral Presentation

On the Crack Propagation by Low Cycle Fatigue in Gray Cast Iron ; T. Noguchi and K. Nagaoka : The 103rd Grand Lecture Meeting of Japan Foundrymen's Society, May 1983

Accelerating Effect of Oxygen on the Growth of Spheroidal Graphite Cast Iron ; M. Sōma and K. Nagaoka : The 103rd Grand Lecture Meeting of Japan Foundrymen's Society, May 1983

Future view of Foundry Industry —from University Laboratory— ; T. Noguchi : The Hokkaido Section Lecture Meeting of Japan Foundrymen's Society, June 1983

Impact Characteristics of S-G Iron with Various Graphite Nodule Diameter ; K. Nagaoka and T. Noguchi : The 104th Grand Lecture Meeting of Japan Foundrymen's Society, Sept. 1983

Fracture Toughness Evaluation of Flake Graphite Cast Iron by the R-Curve Method ; T. Noguchi and K. Nagaoka : The 104th Grand Lecture Meeting of Japan Foundrymen's Society, Sept. 1983

On the Growth Phenomena of Cast Iron in Air of Various Oxygen Concentration ; M. Sōma and K. Nagaoka : The 104th Grand Lecture Meeting of Japan Foundrymen's Society, Sept. 1983

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Lecturer Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno, Mr. S. Emi,
Mr. Y. Otake, Mr. N. Kameda
and Miss A. Matsuno

Students

K. Ebihara, M. Mukai, K. Mabuchi, T. Shigekuni,
T. Toda, M. Mitsuta, M. Oda
and H. Iwata

Current research in this laboratory is mainly concerned with the anodic oxidation of aluminum, corrosion of iron and steel, analysis of metal and oxide surfaces, and the chemistry of metallic ions in aqueous solutions.

Dr. Konno came back from the Lehigh University, Bethlehem, Pennsylvania, U. S. A. on March of 1983.

The main research projects in progress are as follows :

(1) The stability of oxide films on aluminum.

The deterioration of anodic oxide films on aluminum are examined in neutral solutions containing different amounts of anions. The deterioration process has been classified into three groups ; a) hydration, b) dissolution, and c) dissolution with the formation of hydrous oxide.

(2) Formation mechanism of porous anodic oxide films on aluminum.

Porous type anodic oxide films are formed on aluminum in oxalic acid solution under different temperatures, current densities, and the concentrations of oxalic acid to examine the morphology and the density of the films using electron microscopy, gravimetry, and electrochemical measurements. It has been found that the anodizing potential, i. e. the electric field in the barrier layer, is responsible for the film geometry.

(3) Anodizing of Al-Si and Al-Cu alloys.

Al-Si and Al-Cu alloys were anodized in a sulfuric acid solution to examine the structure of porous oxide films with TEM and EDAX.

(4) Removal of radioactive contamination in nuclear power plants.

Spherical magnetite particles, of narrow size distributions, are prepared as a model corrosion product, and the dissolution of magnetite in solutions containing chelating agents are being examined. The dissolution behavior will be compared with that of the real corrosion products formed on iron coupons.

(5) Characterization of MnO_2 as a dry cell material.

Attemps are being made to characterize MnO_2 samples by examining the adsorption of Zn^{2+} ions in slightly acidic and near netral solutions. An adsorption isotherm which describes the adsorption behavior was established. The parameters included in the isotherm are expected to be a good indication of the properties of MnO_2.

(6) Corrosion of iron in high temperature water.

The corrosion rate of iron in pure, high temperature water is measured by gravimetry, and the surface oxide films formed are examined by XPS, and X-ray diffraction.

(7) High temperature oxidation of stainless steel in a moist atmosphere.

Oxidation behavior of Fe-16Cr stainless above 1000°C is followed by an electric balance under different oxygen partial pressures, and water vapor pressures.

(8) Anodizing of steel with organic compounds.

Carbon steel specimens were anodically treated in a neutral borate solution containing small amount of organic compounds. Compositions and protective abilities of the resulted surfaces were examined.

Oral Presentation

Stability of anodic oxide films on aluminum immersed in aqueous solutions —Effects of anions— ; M. Mukai, H. Takahashi and

M. Nagayama: The 9th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1983.

Chemical composition of porous anodic oxide films formed on aluminum in sulfuric acid solutions; K. Ebihara, H. Takahashi and M. Nagayama: *ibid.*, Jan. 1983.

Composition of surface films formed on aluminum by different polishing treatments; H. Takahashi and M. Nagayama: The 18th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1983.

A new method for developing a corrosion-resistant surface on steel; H. Leidheiser, and Jr., H. Konno: Review on ONR corrosion control program, Jan. 1983.

Adsorption of Zn^{2+} ions on MnO_2; K. Sasaki, H. Tamura and M. Nagayama: The 1983 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb. 1983.

Anodizing of aluminum covered with hydrous oxide films; H. Takahashi: Seminar for functional surface films on Al, sponsored by Japan Light Metal Society, Mar. 1983.

Mechanism of adsorption of Zn^{2+} ions on manganese dioxide; H. Tamura, K. Sasaki and M. Nagayama: The 50th Annual Meeting of the Electrochemical Society of Japan, Apr. 1983.

Anodic polarization of porous anodic oxide films on aluminum pretreated in boiling water; M. Koda, H. Takahashi and M. Nagayama: The 67th Meeting of the Metal Finishing Society of Japan, Apr. 1983.

Effects of ion additives on the sealing of porous anodic oxide films on aluminum; M. Koda, H. Takahashi and M. Nagayama: *ibid.*, Apr. 1983.

Interreaction between oxide films on aluminum and anions in aqueous solutions; M. Mukai, H. Takahashi and M. Nagayama: *ibid.*, Apr. 1983.

Distribution of SO_4^{2-} ions in porous anodic oxide films formed on aluminum in sulfuric acid solutions: K. Ebihara, H. Takahashi and M. Nagayama: *ibid.*, Apr. 1983.

Air oxidation of Fe^{2+} ions ; H. Tamura, private seminar at Nippon Steel Co. Apr. 1983.

Surface structure of MnO_2 and the adsorption ability for metal ions ; H. Tamura : The 3rd MnO_2 Symposium, Apr. 1983.

Means for inhibiting the oxygen reduction reaction ; H. Leidheiser, Jr., R. D. Granata and H. Konno : NACE Corrosion Research Symposium, Apr. 1983.

Inhibition of the oxygen reduction reaction using 8-hydroxyquinoline; H. Leidheiser, Jr., H. Konno and A. Vértes : Intl. Conf. Corrosion Inhibition, May 1983.

Passivation of steel in a borate buffer containing organic compounds as a means for improving corrosion resistance; H. Konno and H. Leidheiser, Jr. : The 5th Intl. Symp. Passivity, June 1983.

Corrosion of carbon steel in high temperature water ; H. Takahashi : Summer Seminar of the Hokkaido Corrosion Research Association, Aug. 1983.

Composite oxide films on aluminum ; H. Takahashi and M. Nagayama : The 48th Fall Meeting of Japan Chemical Society, Sep. 1983.

Adsorption of heavy metal ions on metal oxides ; H. Tamura and M. Nagayama : *ibid.*, Sep. 1983.

Adsorption on Zn^{2+} ions on MnO_2 ; H. Tamura and M. Nagayama : The 1st Symposium on Battery Materials, Sep. 1983.

Effect of surface treatment and substrate metal on electrochemical behavior after passivation in a borate buffer containing 8-hydroxyquinoline ; H. Konno and H. Leidheiser, Jr. : Intl. Sym. Fundamental Aspects of Corrosion Protection by Surface Modification, Oct. 1983.

Corrosion of carbon steel in high temperature water ; Y. Horii, K. Mabuchi, H. Konno, H. Takahashi and M. Nagayama : The 24th Corrosion Science Symposium, Sep. 1983.

Impedance analysis of the sealing reaction of porous anodic oxide films on aluminum ; M. Koda, H. Takahashi and M. Nagayama : *ibid.*, Sep. 1983.

Impedance analysis of the hot water hydration of porous anodic oxide films on aluminum ; M. Koda, H. Takahashi and M. Nagayama : The 34th meeting of Intl. Soc. of Electrochemistry.

Electrochemical surface modification of steel with 8-hydroxyquinoline ; H. Konno and H. Leidheiser, Jr. : 30th Ann. Sum. Corrosion and Protection, Nov. 1983.

XPS' study of surface oxide films formed on aluminum by several pretreatments ; H. Takahashi and M. Nagayama : *ibid.*, Nov. 1983.

Corrosion of carbon steel in high temperature water and the structure of surface oxide films ; K. Mabuchi, Y. Horii, H. Konno, H. Takahashi and M. Nagayama : *ibid.*, Nov. 1983.

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

Prof. Dr. K. Nishida, Assist. Prof. K. Atarashiya,
Dr. T. Narita, Dr. K. Kurokawa, Mr. K. Sugawara
and Mrs. Y. Abe

Students

T. Katayama, A. Kumatoritani, T. Ogisho, K. Onodera,
H. Kato, M. Kishimoto and T. Yoneda

This laboratory is concerned with fundamental studies on the high temperature corrosion of metals and alloys in various atmospheres such as H_2S–H_2 or SO_2, the inter-diffusion in alloys and oxides, and the ceramic-metal bonding. The research subjects in progress are as follows:

(1) Sulfidation: Sulfidation behavior of Incoloy 800 at 973 K–1173 K in low sulfur partial pressures (10^{-1}–10^{-5}Pa) was investigated by using TGM, X-ray, EPMA and SEM–EDAX.

(2) Phase diagram: The equilibrium diagram of the Fe–Cr–S system is being derived experimentally.

(3) Effect of creep on corrosion: The effect of creep on grain boundary sulfidation of Fe–26Cr stainless steel is being investigated in H_2S–H_2 atmospheres. Furthermore, the creep rupture properties in various atmospheres such as O_2, SO_2, HCl, or He are also being investigated.

(4) Corrosion in SO_2 gas atmospheres: The high temperature corrosion test of some stainless steels and Fe–Cr–Ni ternary alloys in SO_2 atmospheres are being carried out to clarify the effect of alloying elements of Cr and Ni.

(5) Inter-diffusion: A series of the vapor-solid diffusion studies is being investigated theoretically and experimentally. Inter-diffusion behavior between Mn_3O_4 powder and single crystal of Al_2O_3 is being studied with Pt-marker at high temperature.

(6) Ceramic-metal bonding: Bonding experiments between Si_3N_4 and Fe-26Cr stainless steel using Ti and Ni sheets as a filler are being carried out in He gas atmosphere over the temperature range of 1250-1350°C. The relationship between the bonding strength and the reaction products is discussed.

Oral Presentation

Effect of Selective Sulfidation on the Formation of Internal Sulfidation Layer; T. Narita and K. Nishida: The 18th Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1983

High Temperature Corrosion of Some Metals in SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: The Spring Meeting of the Japan Inst. Met., April, 1983

Sulfidation Behavior of Incoloy 800 at High Temperatures; T. Katayama, T. Narita and K. Nishida: *Ibid.*, April, 1983

High Temperature Corrosion of M(=Fe, Co, Ni)-Cr-C alloys in Low Sulfur Pressures; T. Narita, Y. Nagase and K. Nishida: *Ibid.*, April, 1983

High Temperature Corrosion of Iron Based Alloys in SO_2 Atmospheres; K. Nishida: '83 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1983

Effect of Cr on High Temperature Corrosion of Alloys in SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: *Ibid.*, May, 1983

Analysis of the Cr-Depleted Zone in the Sulfidation of Fe-Cr Alloys; T. Narita and K. Nishida: *Ibid.*, May, 1983

High Temperature Sulfidation of Iron-Based Alloys; K. Nishida: The Hokkaido Section Meeting of the Japan Inst. Met., June, 1983

Study on Ceramic to Metal Bondings —Si_3N_4-SUS304 Bondings—; T. Narita, M. Kawasaki and K. Nishida: *Ibid.*, June, 1983

High Temperature Sulfidation Behavior of Incoloy 800 (II): T. Katayama, T. Narita and K. Nishida: *Ibid.*, June, 1983

High Temperature Corrosion of SUS 316L in SO_2 Atmospheres

(II); K. Kurokawa, T. Narita and K. Nishida: *Ibid.*, June, 1983

High Temperature Corrosion of Some Stainless Steels in SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: The 123rd Committee on Heat Resisting Metals and Alloys, Japan Society for the Promotion of Science, July, 1983

Corrosion Behavior of Iron Based Alloys in SO_2 Atmospheres; K. Nishida, K. Kurokawa and T. Narita: Gordon Research Conference (New London), July, 1983

Sulfidation Properties of Chromium and Diffusivity of Chromium Sulfide; T. Narita and K. Nishida: Ibid., July, 1983

High Temperature Sulfidation of Iron Based Alloys; T. Narita: Corrosion Seminar Sponsored by the Hokkaido Corrosion Research Association, Aug., 1983

Effect of Ni/Cr Concentration Ratio on Corrosion Behavior of Iron Based Alloys in SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: The Autumn Meeting of the Japan Inst. Met., Oct., 1983

Sulfidation and Reduction Behavior of Chromium Sulfide; T. Narita, T. Kanayama and K. Nishida: *Ibid.*, Oct., 1983

Effect of the Internal Sulfidation on the Sulfidation Rate of Alloys; T. Narita and K. Nishida: *Ibid.*, Oct., 1983

Study on Si_3N_4 to Stainless Steel Bondings; T. Narita and K. Nishida: *Ibid.*, Oct., 1983

Sulfidation Behavior of Fe-Cr Alloys in Low Sulfur Pressures; T. Narita and K. Nishida: The 30th Meeting of the Japan Society of Corrosion Engineering, Nov., 1983

Relationship Between the Sulfide Formation and the Corrosion Rate of Iron Based Alloys in SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: The Hokkaido Section Meeting of the Japan Inst. Met., Nov., 1983

Study on Amount and Size of the Oxide Particle for Strengthening of the Sintered Iron Sheet; Y. Suzuki, T. Tsurue, T. Okutani, F. Goto and K. Nishida, *Ibid.*, Nov., 1983

The Air Oxidation of Iron (II) in the Presence of Copper (II) and Iron (III) Oxide Hydrate

Hiroki Tamura, Kazuo Sato
and Masaichi Nagayama

Journal of the Chemical Society of Japan
No. 10, 1405 (1983)

The rates of air oxidation of iron (II) in solution were measured in the presence of copper (II) and/or iron (III) oxide hydrate at a fixed pH. The rate equation obtained for solutions containing iron (III) oxide hydrate but not copper (II) was :

$$-\mathrm{d}\,[\mathrm{Fe\,(II)}]/\mathrm{d}t = k_1\,[\mathrm{Fe\,(II)}]\cdot P_{\mathrm{O}_2} \qquad (1)$$

where [Fe (II)] denotes the total concentration of all the iron (II) species in the system. The equation obtained for solutions containing copper (II) but not iron (III) oxide hydrate was :

$$-\mathrm{d}\,[\mathrm{Fe\,(II)}]/\mathrm{d}t = k_2\,[\mathrm{Fe\,(II)}]^2\cdot P_{\mathrm{O}_2} \qquad (2)$$

The rate constants k_1 and k_2 were found to increase with the concentrations of iron (III) oxide hydrate and copper (II), respectively, and hence they catalyse the reaction.

Provided that the rate of oxidation in the presence of both copper (II) and iron (III) oxide hydrate is expressed as the sum of the rates of (1) and (2), the following equation is obtained :

$$\frac{1}{k_1}\ln\frac{[\mathrm{Fe\,(II)}]_0(k_1+k_2\,[\mathrm{Fe\,(II)}])}{[\mathrm{Fe\,(II)}]\,(k_1+k_2\,[\mathrm{Fe\,(II)}]_0)} = P_{\mathrm{O}_2}\cdot t \qquad (3)$$

where $[\mathrm{Fe\,(II)}]_0$ is the initial value of [Fe (II)]. With the values of k_1, k_2, P_{O_2} and $[\mathrm{Fe\,(II)}]_0$, the theoretical [Fe (II)] vs. time relationship was calculated from eq. (3), and it agreed well with the experimental results.

The catalytic action of iron (III) oxide hydrate and copper (II) was explained in the following way. For iron (III) oxide hydrate a small portion of iron (II) is adsorbed, and the oxidation proceeds

via the adsorbed species. In the presence of copper (II) a small amount of copper (I) is formed by the redox reaction between iron (II) and copper (II), and this copper (I) initiates the reaction between iron (II) and oxygen.

The proposed mechanism gave quantitative explanation of the dependence of the oxidation rates on the concentrations of iron (II), iron (III) oxide hydrate and copper (II), and the partial pressure of oxygen. (Japanese)

Adsorption of Co^{2+} Ions on Spherical Magnetite Particles

Hiroki Tamura, Egon Matijević
and Louis Meites

Journal of Colliod and Interface Science
92, 303 (1983)

The amount of adsorption of Co^{2+} ions on spherical magnetite particles was measured as a function of the pH (5.5∼8.0), the concentration of Co^{2+} ions ($1.7 \times 10^{-8} \sim 1.7 \times 10^{-4}$ mole dm^{-3}), the ionic strength ($I = 10^{-4} \sim 10^{-1}$ mole dm^{-3}), and the temperature (25∼75°C). The amount of adsorption was found to increase with increasing pH, equilibrium concentration of Co^{2+} ions, and temperature, and with decreasing ionic strength. Acid-base titrations of magnetite dispersions were carried out to estimate the number of surface sites of $-FeOH$, $-FeOH_2^+$, and $-FeO^-$ types as a function of pH. The adsorption behavior can be explained quantitatively by considering a surface complex to form at the neutral site ($-FeOH$), combined with the release of one or two protons: $Co^{2+} + -FeOH \rightleftharpoons -FeOCo^+ + H^+$, K_1°; $Co^{2+} + 2\text{-}FeOH \rightleftharpoons -(FeO)_2Co + 2H^+$, β_2°. The values of the equilibrium constants K_1° and β_2°, which pertain to a surface on which the amount of cobalt is negligible, were found to be 3.6×10^{-3} and $3.4 \times 10^{-2}\,dm^{-2}$ at 25°C, respectively. (English)

A Two-Step Anodization Process for Inhibition of the Oxygen Reduction Reaction on Iron

H. Leidheiser, Jr. and H. Konno

Journal of the Electrochemical Society
130, No. 4, 747 (1983)

Anodization of iron by a two-step procedure, first in a borate solution, and second, in a borate solution containing 8-hydroxyquinoline, results in a surface which is inactive for the oxygen reduction reaction, and which has good corrosion resistance in chloride media. The anodized surface also exhibits good resistance to the disbondment of an organic coating under an applied cathodic potential. It is conjectured that the anodized surface consists of a very small amount of surface oxide, possibly a layer of a ferric complex of 8-hydroxyquinoline, and an outer layer of unreacted 8-hydroxyquinoline. (English)

Passivation of Steel in a Borate Buffer Containing Organic Compounds as a Means for Improving Corrosion Resistance

H. Konno and H. Leidheiser, Jr.

Passivity of Metals and Semiconductors,
p. 607 (1983)

Nineteen organic compounds have been identified which yield a corrosion-resistant surface on iron after a two-step anodization process in borate media. Surface analysis techniques have been employed in order to understand the structure of the passive film. (English)

Potential-pH Diagram of Composition/Structure of Passive Films on Iron

Rokuro Nishimura* and Norio Sato**

J. Japan Inst. Metals, 47, No. 12, 1086 (1983)

The composition, layer structure and thickness of the passive films formed on iron in borate and phosphate solutions have been examined as functions of pH, potential and film formation procedure (one-step and two-step oxidation) by using electrochemical and ellipsometric techniques.

The ellipsometric measurements of δP-δA curve during galvanostatic-cathodic film reduction show that the layer structure of the passive film changes with pH from an outer barrier layer/an inner barrier layer in acid to a deposit layer/an outer barrier layer/an inner barrier layer in weak acid and to a deposit layer/a barrier layer in neutral and alkaline solutions. The barrier layer consists of two layers in the pH region below pH 5.5, but turns to be a single layer above this pH. The barrier layer thickness increases nearly linearly with potential, but once the overpotential is fixed, it remains constant regardless of pH, anion species and film formation procedure. The deposit layer thickness, which is almost independent of potential, tends to increase with increasing pH up to about pH 8.

Chemical analyses of iron ion dissolved from the film during cathodic reduction show no significant effect on the deposit layer composition ($Z_{\mathrm{Fe}} \fallingdotseq 3.00$) of pH, anion species, potential and film formation procedure except for a decrease in Z_{Fe} at low potential. The mean oxidation valency of the barrier layer, however, varies from $Z_{\mathrm{Fe}} \fallingdotseq 2.33$ to $Z_{\mathrm{Fe}} = 3.00$, depending on pH, anion species, potential and film formation procedure. The results are explained in terms of the ion selective property of the passive film, and the layer structure and composition are summarized in the potential-pH diagrams. (Japanese)

Reflectometry of Iron Passivation Films in Neutral Borate and Acidic Phosphate Solutions

Toshiaki Ohtsuka, Kazuhisa Azumi
and Norio Sato

Passivity of Metals and Semiconductors, edited
by M. Froment Elsevier Science Publishers
B. V., Amsterdam, (1983), p. 199

3P reflectometry was applied to measure the passive oxide film on iron. In neutral solution the refractive index of the film changes at around the Flade potential where the film composition appears to change. As the solution pH decreases, the optical density of the film increases indicating that the film is more dehydrated in the more acidic solution. The absorption spectrum of the film shows two absorption edges at 2 eV and at 2.6 eV corresponding to two electron energy gaps in the passive film. (English)

A Spectroscopic Property of the Passive Film on Iron by 3-Parameter Reflectometry

Toshiaki Ohtsuka, Kazuhisa Azumi
and Norio Sato

Denki Kagaku, **51**, No. 1, 155 (1983)

3-Parameter reflectometry has been applied to the study on spectroscopic property of the thin passive film on iron. There is difference in spectra of complex refractive index of the film, depending on solution pH values and on potential. Tendency of the spectra, however, resembles the spectum of Fe_2O_3 given in references. It is suggested that the passive film is mainly composed of hydrous Fe_2O_3, but its detail composition is different depending on solution pH and potential. (Japanese)

An In-Situ Reflection-Spectroscopic Study Applied to Anodic Oxide Films on Iron, Nickel, and Titanium

T. Ohtsuka, K. Azumi and N. Sato

Journal de Physique, Colloque C10, 191 (1983)

3-Parameter reflectometry is applied to characterize the anodic thin oxide films on iron, nickel, and titanium. The passivation film on iron exhibits the absorption spectrum and hence the transition levels of electron analogous to that of the bulk Fe_2O_3. The passivation film on nickel have no characteristic feature in the optical spectrum, but its extinction index is much dependent on the anodic potential. The anodic oxide film on titanium have a band gap about 3.2 eV, which is comparable to the band gap 3.05 eV of bulk TiO_2. (English)

Optical and Impedance Studies of Nickel Passivation Film in Neutral Solution

Toshiaki Ohtsuka, Kazuhisa Azumi
and Norio Sato

Passivity of Metals and Semiconductors, edited
by M. Forment Elsevier Science Publishers
B. V., Amsterdam, (1983), p. 79

The passive film on nickel was studied by 3-parameter reflectometry and impedance measurements. It was found that the complex refractive index and the dielectric constant of the film increase with the anodic potential of film formation, indicating that the nonstoichiometric composition of the film is potential-dependent. The electrode impedance of passivated nickel consists of a film capacitor and an electric double layer capacitor at the film surface. (English)

Anodic Oxide Film on Cobalt in Weakly Alkaline Solution

Toshiaki Ohtsuka and Norio Sato

J. Electroanal. Chem., **147**, 167 (1983)

The anodic oxide film on cobalt was studied in alkaline solutions at pH 10.0～12.5 by means of in situ ellipsometry combined with electrochemical measurements. In the primary passive potential region more negative than 0.86 V (vs. HESS) the anodic film is a single CoO layer about 2 nm thick at pH 10.0 but it becomes a bilayer comprising an inner CoO layer about 2 nm thick and a gelatinous $Co(OH)_2$ overlayer 10～20 nm thick in the pH range more basic than pH 11.0. The anodic film in the secondary passive and oxygen evolution potential regions more positive than 0.86 V is composed of an inner CoO layer and an outer $Co_{3-\Delta}O_4$ later. Depending on the non-stoichiometry, the complex refractive index of the outer layer changes from $\bar{n}=3.2-0.5\,i$ for Co_3O_4 ($\Delta=0$) to $\bar{n}=3.2-0.95\,i$ for $Co_2O_3\left(\Delta=\frac{1}{3}\right)$. The outer $Co_{3-\Delta}O_4$ layer thickness increases almost linearly with potential until it becomes almost constant in the transpassive potential region. (English)

Depth-Composition Profiles of Iron-Base Alloy Surfaces Anodically Oxidized in Concentrated NaOH Solution

Masahiro Seo*, Yuzi Sera** and Norio Sato*

J. Japan. Inst. Metals, 47, 752 (1983)

The depth-composition profiles of Fe–30Cr alloy, a series of Fe–Ni alloys, SUS 304 and 316 austenitic stainless steels anodically oxidized at room temperature in deaerated 10.7 mol•kg^{-1} NaOH solution were measured by simultaneous use of Auger electron spectroscopy and argon ion sputter-etching techniques. Chromium is enriched in the passive film formed on Fe–30Cr alloy. A rather thick film (9∼28 nm) with a chromium-depletion zone extending to the substrate grows on Fe–30Cr alloy during short polarization time (5∼15 min) in the transpassive region where chromium dissolves into solution. The effective thickness of chromium-depletion zone, δ (12∼25 nm), in the substrate of Fe–30Cr alloy increases with increasing polarization time in the transpassive region. Assuming that the steady state of selective dissolution of chromium was established, the recession velocity, u ($10^{-10}\sim10^{-9}$ cm•s^{-1}) of the film/substrate interface during transpassive dissolution was estimated, and further the interdiffusion coefficient, $\tilde{D}$ (10^{-15} cm^2•s^{-1}) of Fe–30Cr alloy, which was extremely large as a value at room temperature, was obtained from the approximate relation, $\delta \simeq \tilde{D}/u$.

Nickel-enrichment ranging from the uppermost surface to the alloy substrate was always observed for a series of Fe–Ni alloys anodically oxidized in the passive, transpassive or secondary passive potential region of nickel. Particularly, nickel enrichment is significantly enhanced on the uppermost surface and at the film/substrate interface, which may be attributed to anodic deposition of nickel once dissolved and to selective dissolution of iron, respectively. The thickness (2–4 nm) of the anodic oxide film formed on a series of Fe–Ni alloys decreases with increasing bulk nickel content, indicating the improvement of corrosion resistance due to nickel-enrichment. The effective thickness of nickel enrichment layer, δ (6～10 nm), in the substrate exhibits both the potential- and alloy composition-dependence, suggesting the importance of interdiffusion process in the vicinity of the alloy surface for anodic oxidation of a series of Fe-Ni alloys.

The addition of nickel supresses the transpassive dissolution of chromium and contributes to improvement of the corrosion resistances of SUS 304 and 316 austenitic stainless steels in concentrated NaOH solution. (Japanese)

Surface Analyses of Anodic Oxide Films Formed on Fe-3% Ti Alloy

Masahiro Seo and Norio Sato

Electrochim. Acta, 28, No. 5, 723 (1983)

Surface analyses of the anodic oxide films formed on Fe-3% Ti alloy in deaerated pH 3.0 phosphate solution were performed with Auger electron spectroscopy (AES) and ellipsometry to evaluate the role of alloying titanium in the corrosion resistance of iron.

The 3%-addition of titanium reduced significantly the passivity-maintaining current density of iron as well as the maximum-active current density. Auger analysis revealed that titanium was enriched markedly in the anodic oxide films formed on Fe-3% Ti alloy and that a significant amount of phosphorus was distributed in the whole range of film thickness. Both the amount of titanium enriched in the film and the film thickness (20～40 nm) ellipsometrically obtained were proportional to the amount of electric charge required for passivation. Atomic absorption analysis of the solution indicated that the formation of a titanium-enriched film resulted from a preferential dissolution of iron as ferrous ions.

From the measurement of the potential decay curves of the Fe-3% Ti alloy and pure iron electrodes passivated for different hours, it was concluded that the titanium-enriched layer promoted the passivity by suppressing, though incompletely, the active dissolution, whereas the substantial passivity of the alloy was attributed to the iron oxide film of barrier type formed at the interface of titanium-enriched layer/alloy substrate. (English)

Current-Voltage Characteristics and Oxide Formation of Bipolar $PbSO_4$ Precipitate Membranes

Masao Sakashita, Sakae Fujita and Norio Sato

J. Electroanal. Chem., **154**, 273 (1983)

The current-voltage curves were measured of bipolar precipitate membranes of $PbSO_4$ which separate a $Pb(NO_3)_2$ solution (I) from a H_2SO_4 solution (II) by using a membrane potentiostat. The anodic current, which is carried by H^+ and Pb^{2+} migrating from solution I to solution II and by HSO_4^- and SO_4^{2-} migrating in the opposite direction, is suppressed compared with the cathodic current, which is carried by NO_3^- and H^+. Addition of Ca^{2+} and A^{3+} in the solutions results in an increase of the anodic current. The anodic current-voltage curve can be divided into three regions ; the limiting current region where no membrane composition change occurs, the region where the anodic current gradually increases with voltage and the membrance thickens, and the region where the anodic current increases steeply with voltage and $PbSO_4$ is oxidized PbO_2 in the membrane. (English)

Structure and Density of Anodic Oxide Films Formed on Aluminum in Oxalic Acid Solutions

K. Ebihara, H. Takahashi and M. Nagayama

J. Metal Finish. Soc. Japan, **34**, 548 (1983)

Electropolished 99.99% Al foil coupons were galvanostatically anodized in $C_2H_2O_4$ solutions by applying a fixed amount of charge (7.2 Coulombs/m^2). The morphology of the formed oxide (cell size, 2R, pore diameter, 2r and barrier layer thickness, δ_b) was examined as functions of the acid concentration (2～8%), temperature (10～40°C) and current density (1～180 Am^{-2}), by using electronmicorscopy and electrochemical techniques developed in a previous investigation. The morphology of the oxide films is solely the function of the anodizing voltage, E_a, while E_a is affected by the solution concentration, temperature and anodizing c. d. The density of oxide, ρ, is estimated to be 3.0～3.5, as being the weight of film divided by the volume of oxide. The value of ρ was found to increase with decreasing c. d. and increasing temperature and solution concentration. (Japanese)

Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water

III. Analysis of the Dissolution Characteristics of Hydrated Films by Impedance Measurements

M. Koda, H. Takahashi and M. Nagayama

J. Metal Finish. Soc. Japan, **34**, 44 (1983)

Porous anodic oxide films formed in an oxalic acid solution were hydrated to various extents by allowing them to react with hot water at 99.5°C. The films were then dissolved in a chormic acid-phosphoric acid solution and the dissolution was followed by impedance measurements in a neutral borate solution. The results were analyzed by plotting the log of the absolute value of impedance against the log of frequency. The equivalent circuit of the hydrated film was found to consist of the capacitance of the barrier oxide layer (C_b) combined in series with a parallel combination of the capacitance and resistance components of the hydrous oxide formed in the pores (C_h and R_h). The values of C_b^{-1}, R_h and C_h^{-1} and the their variation with the dissolution time (t_d) were determined. It was found for the films filled up with the hydrous oxide that the film-dissolution proceeds uniformly from the outside at a rate controlled by the dissolution of hydrous oxide, the dissolution rate decreases with the time of the reaction with hot water (t_h). The outermost part of the hydrous oxide formed at $t_h > 30$ min was very resistant to acid-dissolution. It was recognized that the decrease in dissolution rate is always accompanied by an increase in the specific resistance of the hydrous oxide. The barrier oxide layer next to the metal begins to dissolve at the time when the outer part of the film containing the hydrous oxide in the pores is completely dissolved. The dissolution characteristics of the barrier layer itself is little affected by the hot water treatment. These findings agree quite well with the results of a previous investigation conducted by gravimetry. (Japanese)

Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water

IV. Analysis of the Film Structure by Gravimetry and Porefilling Method

Mitsuru Koda, Hideaki Takahashi,
and Masaichi Nagayama

J. Metal Finish. Soc. Japan. **34**, 460 (1983)

Porous anodic oxide films formed on Al in an oxalic acid solution were hydrated for various periods by reaction with hot water. As reported earlier, the hydrous oxide is formed on the entire surface of the pore-walls to fill up the pores in about 10 min, and then the hydration slowly continues from the outer surface so that the outermost part of the film becomes completely hydrated. Using gravimetric data and assuming the composition and density of the hydrous oxide to be $Al_2O_3 \cdot 2H_2O$ and 2.6, the thickness of the fully hydrated portion of the film, H_{hy}, the thickness of the film portion containing the unhydrated pore-wall, H_{ox}, and the thickness of the unhydrated pore-wall δ, were calculated. In another series of experiments, the hydrated films were re-anodized with constant currents, i_r, of 0.01 and 0.5 mA/cm^2 in a neutral borate solution to examine potential-time characteristics. For the smaller anodizing current, the steady potentials are related to the thicknesses of the barrier layers remaining unhydrated; they agree well with those estimated from capacitance measurements. Re-anodizing with the larger current causes dehydration of the hydrous oxide in the pores at the barrier layer-hydrous oxide layer interface, and voids produced by the dehydration are filled up with new oxide formed by the transport of Al^{3+} ion through the barrier layer. The growth of the barrier layer is reflected in the voltage-time characteristics. The transport number of Al^{3+} ion, $T_{Al^{3+}}$, was found to be 0.24. Using this value, H_{ox} was estimated from the voltage-time curve. The values of H_{ox} obtained as function of the hydration time, t_h, were in good aggreement with those estimated by gravimetry. (Japanese)

Selective Surface Oxidation of Fe-30% Ni Alloy

Masahiro Seo and Norio Sato

Proceedings JIMIS-3 : High Temperature Corrosion
Transcations of the Japan Institute of Metals,
Supplement (1983), p. 175

Fe-30 Ni alloy specimens were oxidized for 10 min∼240 min at 433 K∼473 K under a pure oxygen pressure of 1.33×10^4 Pa. The thickness of oxide films was measured by a multiple-angle-of-incidence ellipsometer. The kinetics of film growth was found to obey a parabolic rate law. The depth profiling of oxidized surfaces, performed with simultaneous use of Auger electron spectroscopy (AES) and argon ion sputter-etching technique, reveals that iron component is selectively oxidized and an iron depletion zone is formed in the underlying alloy. The thickness of the iron depletion zone increases with increasing oxidation time or oxidation temperature.

During surface oxidation of the alloy, the transport rate of iron component in the film is almost equal to the interdiffusion rate in the underlying alloy, indicating the establishment of the steady state. The values of interdiffusion coefficient, $\bar{D}$, of the underlying alloy estimated from the depth-composition profiles are more than ten orders of magnitude as large as the values extrapolated from the lattice-diffusion data of the corresponding alloy obtained at high temperature. (English)

Selective Oxidation of Fe-30Ni Alloy in a Low-Temperature Range (433-473 K)

Masahiro Seo and Norio Sato

Oxid. Metals, **19**, No. 3/4, 151 (1983)

Fe-30Ni alloy specimens were oxidized for 10~240 min at 433~473 K in pure oxygen at a pressure of 1.33×10^4 Pa. The thickness of oxide films was measured by a multiple-angle-of-inicidence ellipsometer. The kinetics of film growth were found to obey a paranolic rate law. The depth-profiling of oxidized surfaces, performed with simultaneous use of Auger electron spectroscopy (AES) and argon-ion sputter-etching technique, reveals that iron component is selectively oxidized and an iron-depeletion zone is formed in the underlying alloy. The thickness of the iron depletion zone increases with increasing oxidation time or oxidation temperature. During surface oxidation of the alloy, the transport rate of iron component in the film is almost equal to the interdiffusion rate in the underlying alloy, indicating the establishment of a steady state. The values of the interdiffusion coefficient, $\tilde{D}$, of the underlying alloy estimated from the depth-composition profiles are more than 10 orders of magnitude as large as the values extrapolated from the lattice diffusion data of the corresponding alloy obtained at high temperature. The enormously large values of $\tilde{D}$ may be explained in terms of the vacancy(monovacancy or divancy)-enhanced lattice diffusion mechanism. (English)

High Temperature Sulfidation of Iron and Its Alloys in Low Sulfur Pressures

Keizo Nishida

Proceedings of Third JIM International Symposium
on High Temperature Corrosion
of Metals and Alloys
(Supplement to Transactions of JIM, **24**, 13 (1983))

High temperature sulfidation of iron and its alloys are discussed with results obtained in low sulfur pressures, and compared with the corrosion kinetics and scale morphologies of commercial alloys.

Using Wagner's parabolic rate theory, the corrosion behavior of pure iron is compared with experiments in low sulfur pressures. Based on a similar kinetic theory developed recently for binary alloys with scales following parabolic growth and the difference between the dissociation pressures of ferrous sulfide and other sulfides of the alloying elements, the corrosion behavior is discussed and compared with the expected behavior of the alloy corrosion kinetics.

Commercial alloys such as SUS 316L and SKD 11 were sulfidized in low sulfur pressures and the similar or different results observed with these alloys is evaluated. (English)

Sulfide Formation and Control in High Temperature Corrosion of Iron and Its Alloys in SO_2 Atmospheres

K. Kurokawa, T. Narita and K. Nishida

Proceedings of Third JIM International Symposium
on High Temperature Corrosion
of Metals and Alloys
(Supplement to Transactions of JIM, **24**, 465 (1983))

The scaling kinetics and scale morphology of iron at high temperatures in argon-diluted sulfur dioxide were investigated. The sulfide formation is caused by a local rise in the activity of the sulfur adsorbed on the scale surface, as a result of a rapid consumption of oxygen. It is suggested that the formation of a scale having the lowest possible cation diffusivity is necessary to control the sulfide formation. (English)

Grain Boundary Sulfidation of Fe-Cr Alloys in H_2S-H_2 Atmospheres at High-Temperatures

T. Narita and K. Nishida

Proceedings of Third JIM International Symposium
on High Temperature Corrosion
of Metals and Alloys
(Supplement to Transactions of JIM, 24, 457 (1983))

The sulfidation properties of Fe-Cr alloys were investigated at 1073 and 1173 K in H_2S-H_2 gas mixtures with low sulfur pressures by TGM, X-RAY DIFFRACTION, EPMA, and SEM-EDAX. Significant grain boundary sulfidation emerged from below the surface scale formed on Fe-medium Cr alloys at 1073 K under sulfur partial pressures below the dissociation pressure of ferrous sulfide. At a temperature of 1173 K, a surface scale and copious internal anf grain boundary sulfidation was formed, also for the Fe-high Cr alloys at 1073 K. Both the sulfides formed on the alloy surface and at the grain boundary consisted of (Cr, Fe)S_X phase containing small amounts of iron. It appears that for the initiation of the grain boundary sulfidation there are at least two features : the diffusion flux of the sulfide is much greater than that of alloys, and a selective sulfidation of chromium. Further, sulfidation propagates rapidly by reaction with sulfur and carbides precipitated along the grain boundaries. (English)

High Temperature Corrosion of Some Stainless Steels in SO_2 Atmospheres

K. Kurokawa, T. Narita and K. Nishida

Report of the 123rd Committee on Heat Resisting
Metals and Alloys, Japan Society for the
Promotion of Science, **24**, 353 (1983)

The scaling kinetics and scale morphologies of some commercial steels such as SUS 304L, SUS 316L, SUS 310, and Incoloy 800 were investigated at 1173 K in SO_2 partial pressures of 10^3 and 10^5 Pa by means of TGM, X-ray, EPMA, and SEM-EDAX.

The scale growth of every alloy generally proceeded to obey a parabolic rate law, except for Incoloy 800 in the SO_2 partial pressure of 10^3 Pa, The comparison between the corrosion rates of these steels was performed as a function of the Ni/Cr concentration for each steel. (Japanese)

Fundamental Study on Sulfidation and Protection of Stainless Steel in H_2S-H_2 Atmospheres at High Temperatures

K. Nishida, T. Narita and K. Kitajima

Reports of the Asahi Glass Foundation for
Industrial Technology, **42**, 47 (1983)

The high temperature sulfidation behavior of SUS 316L stainless steel was investigated in detail at 700～900°C in the sulfur partial pressure range of $10^{-1.5}$～10^{-11} atm in order to elucidate the corrosion mechanism of stainless steels in low sulfur atmospheres, because there is an increasing usage of the steels by using fossil fuel in industries.

The result obtained is that the stainless steel showed the preferential sulfidation of grain boundaries of the dissociation pressure of FeS (at the same temperatures), as shown in case of Fe-Cr alloys.

The grain boundary sulfidation is the most important corrosion phenomenon in industries, because the corrosion acceralates the substantial substrate reduction due to internal and grain boundary sulfidations, and sometimes leads to cracking during usage. (Japanese)

Cross-Eye Review on the Mechanical Behaviour of Gray Iron

T. Noguchi

Kinzoku (Metals and Technology), 53, 3, 2 (1983)

Brittle feature in tensile fracture, high strength in bending than in tension, low notch sensitivity and large errors in strength estimation by usual design procedure are the characteristics of gray cast iron, and they are attributed to the graphite flakes distributed in the structure. In this review, the author looked over these characteristics again and showed both experimentally and theoretically that all these characteristics come from the non-elastic or "ductile" behaviour of the material.

The author concluded that the mechanical procedure to estimate the strength based on stress analysis is applicable in cast iron if adequately used. (Japanese)

Why did it Fail ?—Fractography for Failure Analysis

T. Noguchi

Kinzoku (Metals and Technology) 53, 6-9,
2, 42, 47, 30 (1983)

Basic idea of fractography used in failure analysis was explained with many examples of application. Macro and micro fractography gives a lot of information such as the type and the origin of the fracture, the way and the direction of crack propagation, type and magnitude of applied stress, material defects, metallurgical problems, the effects of environments and so forth.

Failure alalysis is completed when these factors obtained from fractography coinside with the material strength and the stress conditions from mechanical analysis. Case studies of ductile, brittle, fatigue and environmental fracture were illustrated with many fractographs and the stress analyses. (Japanese)

On the Notch Strength of Cast Iron

T. Noguchi and K. Nagaoka

Bulletin of the Faculty of Eng., Hokkaido Univ.
112, 35-46 (1983)

In gray cast iron, the strength decreased by notches is much smaller than estimated by elastic formula. In order to clarify the reason for the low notch sensitivity, different cast iron with various strength grades and notch configurations were investigated at room and liquid nitrogen temperature. The finite element method was used to calculate the stress distribution around the notch considering the non-elastic stress strain behaviour of the metal.

According to the stress analysis, the low notch sensitivity is caused by two factors, the non-elasticity of cast iron that reduces the maximum working stress to a much lower value than the elastic estimation, and an over stressed region at the notch root where the stress is higher than the tensile strength of the material.

A fracture criterion with an over stressed depth, δ, was established for the strength evaluation of cast iron under a stress gradient. The value δ is about 3 mm at room temperature and less than 1 mm at liquid nitrogen temperature. These value are related to the metallurgical size of the graphite eutectic cell, and the mechanical conditions of initiation of cracks in cast iron. (Japanese)

Fracture Criterion of Flake Graphite Cast Iron

T. Noguchi

Journ. of the Society of Materials Science, Japan
32, 356, 509-515 (1983)

In this paper, fracture criterion of gray cast iron under non-uniform stress was discussed on the basis of bending and eccentric tension tests performed on the rectangular specimens at room and liquid nitrogen temperatures. The experimental results were analyzed with a concept of "over stressed depth δ".

The value of δ, obtained from the calculated stress distribution at fracture and the tensile strength of the material, were almost constant and 2∼5 mm for both bending and eccentric tension at room temperature, coinciding with those obtained in notched plates and bars. At liquid nitrogen temperature, δ decreased to less than 1 mm, also coinciding with that in notched tension. Thus the constant δ is a vailable as the fracture criterion under the stress gradient conditions.

The value of δ at liquid nitrogen temperature was almost equivalent to the size of a graphite eutectic cell which is considered to be a microstructural unit of cast iron, and at room temperature, increased by 3∼5 times. From the fact that δ depends not only on material but on specimen size or stress gradient and especially on temperature, was infered to be a parameter which represents the propagation condition of a crack before the final fracture. By the concept of over stressed depth, high bending strength, low notch sensitivity of gray cast iron and their dependences on temperature and specimen size, can be explained rationally with a parameter. (Japanese)

Mechanical Properties and Damping Capacity of Grown Cast Iron

M. Sōma and K. Nagaoka

IMONO 55, 4, 199-205 (1983)

Changes of strength and damping characterstic following the growth were examined on flake cast iron and nodular cast iron. As cast iron grows, some voids are formed in it and its strength and density decrease with increasing of the damping capacity. Taking notice of the damping capacity and strength of grown cast iron some industrial uses are expected.

Growth heat-treatment was performed on flake cast iron (FC 20) and nodular cast iron (FCD 50) using specimen of 25 mm dia. and 180 mm length bar by cyclical heating to 950°C and cooling in air. Since after the heatings for 10% linear growth the diameter of unoxidized core of the specimen was about 14 mm in the flake cast iron and about 21 mm in the nodular cast iron, tensile specimen of 7 mm test diameter was taken at the center of the core.

In the flake cast iron grown 4% linearly the tensile strength was 22 kgf/mm^2, and the specific weight was 6.8 with pearlitic structure. The nodular cast iron grown 6～8% linearly kept its tensile strength of 65～75 kgf/mm^2 with increased damping capacity and reduced specific weight of 6.1～6.3. (Japanese)

Quantitative Analysis of Graphite Phase of Grown Spheroidal Graphite Cast Iron

M. Sōma and K. Nagaoka

IMONO 55, 9, 546-551 (1983)

Quantitative analysis of graphite phase in S. G. iron grown up to 10% linearly in air was performed by QTM particle analyzer in order to give metallurgical evidence on the growth theory proposed by the authors.

Distribution pattern of graphite nodule size in ungrown iron was nearly normal with peak of 20～30 μm dia. nodules. With increasing growth number and total fractional area of graphite phase increased linearly. As number of graphite particles below 10 μm size increased remarkably, the curve of nodule size distribution changed gradually to continous J-pattern. After 10% linear growth the largest graphite nodule was 160～170 μm, and the fine particles were increased by 10 times.

Redistribution of graphite in grown nodular cast iron was revealed quantitatively by QTM analysis. The increase of fractional area of graphite should be attributed to the formation of some voids in the grown cast iron, as the quantity of graphite separated in the iron must be constant for the heat treating in the tests. (Japanese)

Changes of Graphite Phase in Grown Ferritic S. G. Cast Iron

M. Sōma and K. Nagaoka

Bulletin of the Faculty of Eng., Hokkaido Univ.,
115, 35-46 (1983)

Cyclical dilatation tests were carried out in vacuum on a nodular cast iron with thermal condition causing complete austenite- ferrite transformation in cooling. The metallographic changes resulted were analyzed by QTM analyzer and were considered on the basis of growth theory due to the irreversible carbon migration in gray cast iron heated.

As growth advanced in the iron by heatings to 950°C increased, total number of graphite increased gradually with marked generation of new fine particles sized beloe 10 μm. On the other hand enlargement of pre-existed graphite was anlyzed quantitatively. Consequently histogram pattern of graphite size in S. G. iron grown was changed from the initial curve with two peaks to a continuous J-shape curve.

When the ferritic nodular cast iron is heated to austenite temperature and then cooled with complete ferritization following the transformation, as the ferrite-austenite phase transformation is reversible phenomenon, the irreversible volume change of growth is only attributed to the carbon migration between graphite and matrix. Analyzed changes in graphite phases of grown nodular cast iron are accounted by the redistribution of graphite due to the irreversible carbon diffusion. (Japanese)

Changes of Graphite Phase in Grown S. G. Iron

K. Nagaoka and M. Sōma

Luzer Reference Series, NIRECO, 13, 1, (1983)

As a link in a chain of experiments on the growth mechanism of cast iron changes of graphite phase in nodular cast iron were analyzed by QTM analyzer (Luzer 450). Two specimens of a nodular cast iron with coarse and fine graphite nodules were made by pouring the Mg-treated iron into a keel block sand mould and a metal mould for a bar. Number of graphite nodules was 90/mm^2, 758/mm^2 respectively. Growth tests were carried out by heating to 950°C for 30 min in air cyclically until the growth reached to linear 8%.

Up to 40 heatings or 3% linear growth, the fine graphite iron grew more than the coarse graphite iron. Finally 8% linear growth was caused by 87 heatings in the coarse graphite iron with accelerated growth rate and by 109 heatings in the fine graphite iron.

Increase of numbers and total fractional area of graphite, generation of fine graphite particles, coarsening of graphite pre-existed were advanced as the iron grew with gradual change of distribution pattern of graphite nodule sizes. Effect of graphite size on the growth of nodular cast iron is accounted by the castoff viod growth theory based on the irreversible carbon diffusion in gray cast iron. (Japanese)

Thermochemical Splitting Cycle of H_2S with Cobalt Sulfide

H. Kiuchi, I. Nakamura and T. Tanaka

J. Min. Met. Inst. Japan, **99**, 1143, 401 (1983)

The thermochemical splitting of H_2S shown below was proposed and experimental studies were made on this cycle.

$$Co_9S_8 + H_2S = 9CoS + H_2 \quad \cdots\cdots\cdots \quad (1)$$

$$9CoS = Co_9S_8 + 0.5S_2\,(g) \quad \cdots\cdots\cdots\cdots \quad (2)$$

$$H_2S = H_2 + 0.5S_2\,(g) \quad \cdots\cdots\cdots\cdots\cdots \quad (3)$$

The decomposition behavior of H_2S into H_2 and S^0 can be determined by following the change in H_2 concentration during reaction (1). Reaction (2) was examined by leaking Ar gas under reduced pressure.

The same formation behavior of H_2 was observed during 40 cycles. Therefore, the cycle proposed here may be considered to be applicable to the recovery of H_2 and S^0 from H_2S. Also, it was found that the thermal decomposition of the sulfurized product was accelerated by leaking Ar gas under reduced pressure and that this method was more effective for the thermal decomposition of cobalt monosulfide than the decomposition in vaccum.

Higher concentration of H_2 and larger amount of the generated H_2 were obtained with increasing H_2S flow rate in reaction (1). In contrast to this, higher conversion of H_2S to H_2 and higher mean concentration of H_2 were observed with decreasing H_2S flow rate. The cycle at a sulfurization temperature of 700°C provided the highest concentration of H_2. whereas, the largest amount of H_2 was generated at the temperature 500 to 600°C.

The thermal efficiency of the present cycle was calculated undre the condition of sulfurization at 600°C and thermal decomposition at 850°C. If the heat of formation or free energy of formation of $H_2O(g)$ is taken as the heat value retained by one mole of the formed H_2 and the heat value of formed elemental sulfur is distegarded, the thermal efficiency for this cycle can be estimated to be about 60%.

Thermochemical Decomposition of Hydrogen Sulfide with Nickel Sulfide

H. Kiuchi, K. Funaki and T. Tanaka

Metallurgical Transactions B., AIME,
14 B, 347 (1983)

In this research, the two-step thermochemical cycle shown below is proposed experimental studies were made on the cycle.

$$\begin{array}{l} Ni_3S_2 + H_2S = 3NiS + H_2 \\ 3NiS = Ni_3S_2 + 0.5S_2(g) \\ \hline H_2S = H_2 + 0.5S_2(g) \end{array}$$

In the case where Ni_3S_2 alone was used without inert additions, nickel sulfide sintered or partly fused due to the melting point depression resulting from the thermal decomposition of formed NiS. Such sintering could be prevented by mixing the nickel sulfide powders with Al_2O_3 or MoS_2. The cyclic reactions were thereby shown to provide a stationary high decomposition rate of H_2S. Polysulfides, such as MS_2, have previously been employed in this kind of cycle. This research showed that the use of lower sulfides such as Ni_3S_2 may be regarded as rather promising based on the thermodynamic investigation of the respective reactions composing the cycle. The comparison between the sulfurization reactions of NiS to NiS_2 and of Ni_3S_2 to NiS further showed that the latter was superior to the former with respect to the kinetics and thermodynamical properties of the reaction.

Hydrogen Reduction of Spent Copper Electrolyte

R. Togashi and T. Nagai

Hydrometallurgy, **11**, 149 (1983)

The recovery of copper powder and the removal of arsenic from spent copper electrolyte by means of hydrogen reduction aimed at purifying the spent cipper electrolyte were studied. About 90% of the copper in the electrolyte could be recovered in the form of pure copper powder after 20 min reduction at 180°C at a hydrogen pressure of 20 kg cm^{-2} (2.0 MPa). An induction period, due to slow hydrogen reduction of As^{5+} to As^{3+}, could be eliminated as a result of the addition of copper powder as a reductant. Arsenic, antimony and bismuth in the liquor have been found to catalyze the hydrogen reduction of copper. When the copper concentration in the treated solution reached a certain low level, copper arsenide, Cu_3As, was formed on the surface of copper through hydrogen reduction of As^{3+} ions. This reaction was very slow and a long reaction time was required for complete removal of arsenic. Therefore, in order to purify spent copper electrolyte, hydrogen reduction.

Removal of Arsenic from Geothermal Hot-Water by Hydrated Zirconium Oxide

T. Nagai and R. Togashi

Report of Special Project Research on Energy under
Grant in Aid of Scientific Research of the
Ministry of Education, Science and
Culture, Japan. 8, 439 (1983)

Removal of zesenic by means of iron-exchange rechnique was studied for the treatment of waste hot-water from geothermal power plants, in order to utilize its thermal energy for multi-purposes use. Specially designed ion-exchangers were used : (a) hydrated zirconium oxide dispersed on a porous carrier for column adsorption tests, and (b) the oxide powder made by means of the Freeze-Melt Process (freezing the colloidal zirconium) hydroxide-precipitates followed by ice-melting) for two-stages counter-current adsorption tests.

Results from laboratory work with a made-up solution which is free from silicic acid were compared with those from tests at a geothermal power plant. There was a large difference caused mainly by the presence of silicic acid in the geothermal hot-water which inhibits the arsenic adsorption, and further work will be required to overcome this inhibition action by silicic acid.

Evaluation of Bipolar Electrode Cell for Electrowinning of Liquid Aluminum from Chloride Melts

T. Ishikawa and S. Konda

Proceedings of the First International Symposium on
Molten Salt Chemistry and Technology,
p. 5-8 (1983)

In order to develop a suitable bipolar electrode cell for saving of energy and to estimate in advance cell voltage and current efficiency at various applied current density during electrowinning, some fundamental principles with calculative procedures of cell efficiency, of which value gives possible maximum of gross current efficiency, was proposed by the use of a modified equivalent circuit of the bipolar electrode cell.

The validity of these principles was also confirmed experimentally by construction and operation of the laboratory-scale cells, about which had been known the following data ; number of the bipolar electrodes in the cell, total sectional area of the cell, average sectional area and thickness of the bipolar electrodes, distances between the electrodes, specific conductivity of the melts and decomposition voltages of aluminum chloride at various concentration of aluminum chloride in the melts at operational temperatures. (English)

Chemically Stimulated Exo-electron Emission and Chemiluminescence from Metal Surfaces

Masahiro Seo

Ionics, No. 93, 60 (1983)

This article reviews chemically stimulated exo-electron emission (CEE) and chemiluminescence (CL) from metal surfaces without any excitation such as X-ray radiation and electron bombardment. CEE and CL from metal surfaces accompanied by adsorption of oxygen or halogen gas usually exhibit an exponential time-decay and are extremely sensitive to the active sites where adsorption reaction preferentially proceeds. CEE from silver catalyst during partial oxidation of ethylene, however, occurs contineously as far as the reaction proceeds. Moreover, the emission rate of CEE from silver catalyst is closely correlated with the conversion rate of ethylene to ethylene oxide.

CEE and Cl are directly related to surface defective structure and localized state of electron. CEE and CL, therefore, will be promising as a powerful tool for in-situ measurement of surface reaction, if the emission mechanism is made clear. (Japanese)