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CORROSION RESEARCH

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HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

K. Kurokawa, K. Imai, T. Katayama, T. Kanayama,
M. Kawasaki, Y. Nagase and J. Fukuoka

This laboratory is concerning with fundamental studies on the high temperature corrosion of metals and alloys in oxygen, sulfur and their mixed oxidant atmospheres, the inter-diffusion in alloys and oxides, and the ceramic-metal bonding. A new research program was commenced for the effect of high temperature corrosion on the creep rupture properties. The research subjects in progress are as follows:

(1) Sulfidation: Sulfidation of the high-carbon Cr alloys have been investigated by using of TGM, X-ray, EPMA and SEM-EDAX to clarify the effect of carbides on the internal and/or grain boundary sulfidation. Sulfidation behavior of Incoloy 800 is also being investigated.

(2) Corrosion in SO_2 gas atmospheres: The high temperature corrosion test of some metals and alloys in SO_2 atmospheres revealed the effects of alloying elements such as Cr, Al and Si on the control of sulfide formation.

(3) Effect of corrosion on creep rupture properties: The effect of high temperature corrosion on the creep rupture properties is being investigated in various atmospheres such as O_2, H_2-H_2S, Ar-SO_2.

(4) Diffusivity of metal ions in sulfides: The diffusivities of metal ions in CrS_X phase and (Fe, Cr)S phase are being investigated by Rosenberg's method.

(5) Inter-diffusion studies: As a series of the vapor-solid diffusion studies, the Ni–Cu system was investigated. Interdiffusion coefficients between Mn_3O_4 powder and single crystal of Al_2O_3 were also determined at high temperatures.

(6) Ceramic-metal bonding: Bonding experiments between Ti-plated Si_3N_4 and SUS 304 using an Al sheet as a filler was carried out in Ar atmosphere at 943 K. The bonding strength was dependent upon the retention time at the bonding temperature.

The Third JIM International Symposium (JIMIS-3) on "High Temperature Corrosion of Metals and Alloys" was held at Hotel Mt. Fuji in the neighborhood of Lake Yamanaka on the foot of Mt. Fuji during four days, Nov. 17–20, 1982. Prof. Nishida, the vice-chairman of this symposium, gave a plenary lecture on "High Temperature Sulfidation of Iron and Its Alloys in Low Sulfur Pressures". Dr. Narita and Mr. Kurokawa also attended this symposium with papers on "Grain Boundary Sulfidation of Fe–Cr Alloys in H_2S-H_2 Atmospheres at High-Temperatures" and on "Sulfide Formation and Control in High Temperature Corrosion of Iron and Its Alloys in SO_2 Atmospheres", respectively.

Before and after the symposium many foreign researchers visited this laboratory. They are Prof. W. L. Worrell of Univ. of Pennsylvania, U. S. A., on 27–31 Oct., Prof. D. J. Young of Univ. of New South Wales, Australia, on 12–14 Nov., Dr. M. J. Graham of National Research Council, Canada, on 21–24 Nov., Prof. S. Mrowec of Institute of Materials Science, Academy of Mining and Metallurgy, Poland, on 23–24 Nov., and Prof. K. N. Strafford of School of Materials Engineering, Newcastle upon Tyne Polytechnic, England, on 24–27 Nov. All of them made very impressive lectures for us and expected to meet us once more somewhere else in future.

Oral Presentation

High Temperature Corrosion of Iron Based Alloys in SO_2 Atmospheres —Sulfide Formation and Its Control—; K. Kurokawa, T. Narita and K. Nishida: The 17th Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1982

Sulfidation at Grain Boundary; T. Narita: The Research Meeting on Steel Materials of the Hokkaido Section of Iron and Steel Inst. Japan, Jan., 1982

Inter-Diffusion in β_2-Phase of the Fe-Ni-Al Ternary Alloy system; T. Yamamoto, T. Takashima and K. Nishida: The Spring Meeting of the Japan Inst. Met., April, 1982

Sulfidation Behavior of the High-Carbon Chromium Steels (I); K. Imai, T. Narita and K. Nishida: *Ibid.*, April, 1982

Sulfidation Behavior of Chromium at High-Temperatures (I); T. Narita, T. Shimawaki and K. Nishida: *Ibid.*, April, 1982

High Temperature Corrosion of Iron in (O_2+SO_2) Atmospheres; K. Kurokawa, T. Narita and K. Nishida: *Ibid.*, April, 1982

High Temperature Corrosion of Some Fe-Cr Binary Alloys in SO_2 Atmospheres; The Hokkaido Section Meeting of the Japan Inst. Met., May, 1982

Study on Ceramic to Metal Boundings (I) —Al_2O_3/Cu/Ni Boundings—; T. Narita, B. Kuzuma and K Nishida: *Ibid.*, May, 1982

Sulfidation Behavior of the High-Carbon Chromium Steels (II); K. Imai, T. Narita and K. Nishida: *Ibid.*, May, 1982

Inter-Diffusion in Ni-Cu System by the Vapor-Solid and Solid-Solid Diffusion Methods; T. Takashima, T. Yamamoto and K. Nishida: *Ibid.*, May, 1982

Study on Al_2O_3 to Ni Bondings; T. Narita: The Research Meeting on Fusion Reactor Materials of the Hokkaido-Kanto Sections of the Japan Inst. Met., June, 1982

High Temperature Sulfidation of Chromium —Kinetics and Scale Structures—; T. Narita and K. Nishida: The 123rd Committee on Heat Resisting Metals and Alloys, Japan Society for the Promotion of Science, July, 1982

Some Aspects on the Preferential Sulfidation at the Grain Boundary of Fe-Cr Alloys; T. Narita and K. Nishida: The Autumn Meeting of the Japan Inst. Met., Sep., 1982

High Temperature Corrosion of a SUS316 Stainless Steel in SO_2 Atmospheres; K. Kurokawa, T. Narita and K. Nishida: *Ibid.*, Sep., 1982

Sulfidation Behavior of Chromium Carbides at High Temperatures ; K. Imai, T. Narita and K. Nishida : *Ibid.*, Sep., 1982

Inter-Diffusion in Al_2O_3-Cr_2O_3 System ; K. Nishida, K. Atarashiya, T. Narita and Y. Ito : *Ibid.*, Sep., 1982

Scanning Auger Microprobe Analysis of the Layer at the Junction of Composit Material : Y. Suzuki, T. Tsurue, T. Narita and K. Nishida : *Ibid.*, Sep., 1982

Inter-Diffusion in the Ni–Cu System by the Vapor-Solid and Solid-Solid Diffusion Methods ; T. Yamamoto, T. Takashima and K. Nishida : *Ibid.*, Sep., 1982

High Temperature Sulfidation of Iron and Its Alloys in Low Sulfur Pressures ; K. Nishida : The Third JIM International Symposium (JIMIS-3), Nov., 1982

Grain Boundary Sulfidation of Fe–Cr Alloys in H_2S-H_2 Atmospheres at High Temperatures ; T. Narita and K. Nishida : *Ibid.*, Nov., 1982

Sulfide Formation and Control in High Temperature Corrosion of Iron and Its Alloys in SO_2 Atmospheres ; K. Kurokawa, T. Narita and K. Nishida : *Ibid.*, Nov., 1982

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Lecturer Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno, Mr. S. Emi,
Mr. Y. Otake, Mr. N. Kameda
and Mrs. H. Akatsuka

Students

M. Koda, K. Ebihara, M. Mukai, K. Mabuchi,
K. Sasaki, T. Shigekuni and K. Takahashi

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's stay at the Lehigh University, Bethlehem, Pennsylvania, U. S. A. has been extended to March of 1983.

The main research projects in progress are as follows:

(1) Anodizing of aluminum in the presence of hydrated oxides.

Aluminum specimens are dipped in high temperature water to form hydrated oxide films, and the specimens are anodized in neutral solutions. The formation of the hydrated oxide and its conversion by anodizing are examined by gravimetry, XPS, and TEM.

(2) 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.

(3) Geometrical structure and density 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.

(4) Hydration of porous anodic oxide films on aluminum in boiling water.

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

(5) Air-oxidation of Fe^{2+} ions in near neutral solutions.

Ferrous ions can be oxidized by air to form Fe (III)-oxyhydroxides in aqueous solutions. The rate of reaction is accelerated by the reaction product as well as the coexisting cations (Cu^{2+}, Co^{2+}) and anions (HPO_4^{2-}, F^-). Some anions (Cl^-, SO_4^{2-}) retard the reaction. The combined effect of Fe-oxyhydroxides and the particular anions or cations on the kinetics of the oxidation of Fe^{2+} ions are being examined in connection with the corrosion of iron and steels.

(6) 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.

(7) 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 believed to be a good indication of the properties of MnO_2.

(8) 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.

(9) High temperature oxidation of stainless steel in a moist

atmosphere.

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

Oral Presentation

Effect of anions on the formation of barrier type anodic oxide films on aluminum; H. Takahashi, Y. Saito and M. Nagayama: The 8th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1982.

Geometrical structure of porous anodic oxide film on Al formed in an oxalic acid solution; K. Ebihara, H. Takahashi, and M. Nagayama: *ibid.*, Jan. 1982.

Acid dissolution behavior of anodic oxide films on Al sealed in a hot water; M. Koda, H. Takahashi and M. Nagayama: *ibid.*, Jan. 1982.

Initial corrosion behavior of mild steel in high pressure hot water; Y. Horii, H. Konno, H. Takahashi, H. Tamura and M. Nagayama: The 17th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1982.

Effects of Cu(II) ions and Fe(III) colloids on the air oxidation of Fe(II) ions in aqueous solutions; K. Sato, H. Tamura and M. Nagayama: The 1982 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb. 1982.

Adsorption of Co(II) ions on magnetite particles; H. Tamura, E. Matijević and L. Meites: *ibid.*, Feb. 1982.

Effect of electrolyte anions on the anodizing of aluminum in neutral solutions; H. Takahashi and M. Nagayama: The 65th Meeting of the Metal Finishing Society of Japan, Apr. 1982.

Changes in the acid dissolution behavior of anodic oxide films on Al by hot water treatment Part I. and II; M. Koda, H. Takahashi and M. Nagayama: *ibid.*, Apr. 1982.

Structure and density of anodic oxide films on Al formed in an oxalic acid solution; K. Ebihara, H. Takahashi and M. Nagayama: *ibid.*, Apr. 1982.

Adsorption of Co(II) ions on spherical magnetite particles; H. Tamura, E. Matijević and L. Meites: The 45th Annual Meeting of the Chemical Society of Japan, Apr. 1982.

Measurements of oxide films; H. Takahashi and M. Nagayama: Seminar on the Fundamental Aspects and Applications of CPA sponsored by the U. S. Office of the Electrochemical Society of Japan, May 1982.

Effects of phosphate concentration and temperature on the formation of anodic oxide films on Al in neutral phosphate solutions; H. Takahashi, G. Hirose and M. Nagayama: The 49th Annual Meeting of the Electrochemical Society of Japan, May 1982.

Air oxidation of Fe(II) ions in the presence of Fe(III)-oxyhydroxides and Cu(II) ions; H. Tamura, K. Sato and M. Nagayama: *ibid.*, May 1982.

Anodic oxide films on aluminum; M. Nagayama: The 1st Lilac Seminar sponsored by the Hokkaido Section of the Electrochemical Society of Japan, June 1982.

Electrons in circuits; M. Nagayama: The Meeting on Chemical Education sponsored by the Hokkaido Section of the Chemical Society of Japan, July 1982.

Effect of a pre-formed Al(III)-oxyhydroxide layer on the anodic oxidation of aluminum; H. Takahashi, T. Miyamoto, N. Fujimoto and M. Nagayama: The 1982 Summer Meeting of the Hokkaido Sections of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, July 1982.

Adsorption of chloride ions on Fe(III)-oxyhydroxides; H. Tamura, N. Ohgane and M. Nagayama: *ibid.*, July 1982.

Effects of CrO_4^{2-}, PO_4^{3-}, and Ni^{2+} ions on the hydration of anodic oxide film on Al in hot water; H. Koda, H. Takahashi and M. Nagayama: *ibid.*, July 1982.

Stability of anodic oxide films on Al in phosphate solutions; M. Mukai, H. Takahashi and M. Nagayama: *ibid.*, July 1982.

Metal oxides as ion adsorptives; H. Tamura: Corrosion Seminar sponsored by the Hokkaido Corrosion Research Association, Aug. 1982.

An explanation for the adsorption behavior of heavy metal ions on Fe (III)-oxyhydroxides ; H. Tamura and M. Nagayama : The 31st Annual Meeting of the Japan Society for Analytical Chemistry, Sep. 1982.

Analysing compositions of anodic oxide films on aluminum by XPS ; H. Takahashi, H. Konno and M. Nagayama : *ibid.*, Sep. 1982.

Electrochemical and other methods for studying corrosion inhibition reactions of significance to polymeric coatings ; H. Leidheiser, Jr. and H. Konno : The Electrochemical Society, Detroit, Michigan, Meeting, Oct. 1982.

A sealing mechanism of porous anodic oxide film on aluminum ; M. Koda, H. Takahashi and M. Nagayama : The 66th Annual Meeting of the Metal Finishing Society of Japan, Oct. 1982.

Anodic oxidation behavior of aluminum pre-treated in hot water ; H. Takahashi and M. Nagayama : *ibid.*, Oct. 1982.

Properties of electrolytic MnO_2 prepared under different conditions ; H. Tamura, S. Emi, K. Sasaki, M. Nagayama and A. Kozawa : The 23rd Battery Symposium in Japan, Nov. 1982.

ENGINEERING MACHINERY MATERIALS LABORATORY

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

Students

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

Professor Nagaoka attended The 49th International Foundry Congress, Chicago, April 14–17 1982, as an official delegate and then he and assistant professor Noguchi attended The 86th AFS Casting Congress, Chicago, April 19–23 1982. At the Gray Iron Seassion of the AFS Congress Dr. Noguchi presented a paper entitled "Strength Evaluation of Cast Iron Circular Plate by Finite Element Method", and the paper had published in the AFS Transactions 82–64.

Subjects of research in this laboratory are as follows :

(1) Low-cycle fatigue strength of sintered steel was examined for tension load with smooth and notched specimens. Decrease of the strength with no notch and blunt notch of factor below 1.5 were about 8% for $N=10^2$, and 19% for 10^4. The decrese of sharp notched specimens was about 20% for $N=10^2$ and 40% for 10^4 and the decreases were almost saturated with factor of notch above 2.5.

(2) Tensile strength of sintered steel was tested statistically with strain-gauge method. Not only the strength but also the stress strain curves scattered widely. The fracture strength were within 10.5 to 29.1 kgf/mm^2, though the average was 21.7 kgf/mm^2. With specimens of normal weight and sectional area the tensile strength showed Weibull distribution, but fracture strain and elastic modulus showed normal distribution.

(3) Fracture toughness of cast iron was examined by ASTM Standard for K_{Ic}, JSME Standard for J_c and R-Curve method for J_c by unloading compliances. Each method have some factors for error theoretically and practically, though a reliable value may be obtained by R-Curve method where J_{in} is defined as a critical J_{Ic}.

(4) Propagation of low-cycle fatigue cracks in flake graphite iron was observed optically and analyzed with COD-curves for bending of notched beams. An equivalent crack length a* obtained from P–COD compliance is available for the $da/dN=C(\Delta K)^m$ relation. The value of factor m may be nearly constant of 6 to 8, though the value of C varies with the grade of iron and the stress ratio.

(5) Analysis of graphite phase by Q. T. M. was applied on the mechanical properties of cast iron. Before the impact test of S. G. irons with various nodule size, three dimensional distribution and average size of graphite nodules were determined by the calculation with Saltykov method. Results of the instrumented impact test for load-time curves showed that the impact energy and the transition temperature depended mainly on the onset of rapid propagation of cracks.

(6) Strength after repeated full annealing was tested on cast irons with fine and coarse graphite flake. The fine flake iron was alloyed with 0.38% Ti. Tensile strength after the first annealing was about 75% of as-cast iron, because of the change of matrix from pearlite to ferrite. By added annealing of a few cycles the strength did not decrease, though the specific weight and hardness decreased gradually.

(7) Growth test of cast iron had carried continuously in the heating atmosphere of air reduced oxygen by the oxygen-pump. Growth increased remarkably by low concentration of oxygen not only in flake graphite iron but also in S. G. iron heated in austenite region. Holding at 950°C for 30 min during heating and cooling of from 800°C to 950°C promoted the growth of S. G. iron in the air of more than 2% of oxygen.

Oral Presentation

Strength Evaluation of Cast Iron Circular Plate by the Finite Element Method; T. Noguchi and K. Nagaoka: The 86th AFS Casting Congress (Chicago), April 1982

Effect of Oxygen Concentration in Air on the Growth of Flake Graphite Cast Irons in the Austenite Region; M. Sōma and K. Nagaoka: The 101st Grand Lecture Meeting of the Japan Foundrymen's Society, (Tokyo) May 1982

Estimation of J-Integral in Cast Iron by FEM; T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society (Hakodate) July 1982

Low-cycle Fatigue of Cast Iron; K. Ōkubo, T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society, (Hakodate) July 1982

Three Dimensional Distribution of Graphite Nodules in S. G. Iron; T. Narita, T. Noguchi and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society, (Hakodate) July 1982

Effect of Low-concentration Oxygen on the Growth of Cast Iron; M. Sōma and K. Nagaoka: The Hokkaido Section Lecture Meeting of the Japan Foundrymen's Society, (Hakodate) July 1982

The Effect of Graphite Size on the Growth of S. G. Iron; M. Sōma and K. Nagaoka: The 102nd Grand Lecture Meeting of the Japan Foundrymen's Society, (Fukuoka) Oct. 1982

Introduction of Fractography (Basis and Applications); T. Noguchi: Goverment Industrial Research Institute, Nagoya, Oct. 1982

Is Gray Iron Brittle? —Cross-Eyed Review on Mechanical Properties of Cast Iron—; T. Noguchi: The Tōkai Section Meeting of Research of the Japan Foundrymen's Society, (Nagoya) Oct. 1982

NONFERROUS EXTRACTIVE METALLURGY LABORATORY

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

Students

R. Togashi, Y. Nakai, G. Kano, N. Inaba,
T. Tanimura and M. Miyakawa

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.

i) Thermochemical splitting of hydrogen sulfide.

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

$$\begin{array}{l} MS_x + H_2S = MS_{x+1} + H_2 \\ MS_{x+1} = MS_x + S^\circ \\ \hline H_2S = H_2 + S^\circ \end{array}$$

ii) Hydrogen production with water and metal sulfides.

Reactions between steam and a metal sulfide such as Ag_2S, CaS, and FeS are being tested within the temperature range 700～1000°K.

(2) Use of hydrogen to the treatment of sulfide ores and metallurgical products.

i) Reduction of metal sulfide ores with hydrogen.

Kinetic studies on the direct reduction of sulfide ores with lime are being made.

ii) Reduction of metal sulfates with hydrogen.

As hydrogen reduction of metal sulfates prceeds under a relative lower temperature as 300°C, the utilization of waste heat or solar energy for metallurgy will be expected.

iii) 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

Recovery of Hydrogen from Hydrogen Sulfide with Nickel Sulfide; T. Tanaka and H. Kiuchi: Annual Meeting of the Research Group for Chemical Energy, Grant in Aid for Scientific research, The Ministry of Education, Jan. 1982.

A Study on Metallurgical Application of Pyro-hydrolysis of $FeCl_2$; T. Tanaka and R. Shibayama: Research Committee for New Treatments of Sulfide Ores, Min. Met. Inst. Japan, Feb. 1982.

A Study on Effective Utilization of Hydrogen Sulfide (8th Report); H. Kiuchi, Y. Nakai and T. Tanaka: Annual Meeting Min. Met. Inst. Japan, April 1982

Fundamental Studies on the Reaction between Metal Chloride and

Steam (III); R. Shibayama, T. Mohri and T. Tanaka: *ibid.*, April 1982.

Sulfidizing of Copper Electrolyte using Sodium Hydro-Sulfide; T. Nagai and R. Togashi: *ibid.*, April 1982.

Hydrogen Pressure Reduction of Copper Electrolyte (II); R. Togashi and T. Nagai: *ibid.*, April 1982.

Thermodynamical Studies on the Bi-S Binary Melts; H. Kiuchi, Y. Nakai and T. Tanaka: Annual Meeting of the Hokkaido Section, Min. Met. Inst. Japan, June 1982.

Removal of Arsenic in Copper Electrolyte by Solvent Extraction; G. Kanoh and T. Nagai: *ibid.*, June 1982.

Hydrogen Pressure Reduction of Copper Electrolyte; R. Togashi and T. Nagai: *ibid.*, June 1982.

A Purification Process for Spent Copper Electrolyte; G. Kanoh, R. Togashi and T. Nagai: *ibid.*, June 1982.

Thermochemical Decomposition of H_2S with Nickel Sulfide; H. Kiuchi, K. Funaki, Y. Nakai and T. Tanaka: World Hydrogen Energy Conference IV, Pasadina, California, USA, June 1982.

A Study on the Recovery of Hydrogen from H_2S with Ni-Co-Cr Ternary Sulfides; H. Kiuchi, K. Funaki, T. Ohmi, S. Tasai and T. Tanaka: The 1982 Summer Meeting of the Hokkaido Section, Japan Chem. Soc., July 1982.

Purification of Spent Copper Electrolyte by Solvent Extraction —Hydrogen Reduction-Sulfides Precipitation.—; G. Kanoh, R. Togashi and T. Nagai: Fall Meeting of the Min. Met. Inst. Japan, Oct. 1982.

Recovery of Hydrogen and Elemental Sulfur from Hydrogen Sulfide (VI); H. Kiuchi, N. Inaba, S. Tasai and T. Tanaka: The Fall Meeting of the Hokkaido Section, Min. Met. Inst. Japan, Oct. 1982.

Thermodynamical Studies on the Bi-S Binary Melts; H. Kiuchi, Y. Nakai and T. Tanaka: *ibid.*, Oct. 1982

Solvent Extraction of Arsenic in Spent Copper Electrolyte; G. Kanoh and T. Nagai: *ibid.*, Oct. 1982.

Removal and Recovery of TBP in a Raffinate by Carbon Tetrachloride-Scrubbing; G. Kanoh, R. Togashi and T. Nagai:

Symposium on Solvent Extraction, Dec. 1982.

Removal of Arsenic from Hot Waste from Geothermal Power Plants; T. Nagai, R. Togashi and T. Tanimura: Annual Meeting of the Research Group for Natural Energy, Grant in Aid for Scientific Research, The Ministry of Education, Dec. 1982.

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

T. Suzuki, K. Ogura, N. Sato, Ka. Ito, Ku. Ito,
M. Taniguchi and K. Narita

Prof. H. Ohashi went abroad on August 1982 to work with Prof. O. R. Olander at the University of Carifornia, Berkeley. His return is scheduled on December 1983. Dr. M. Moriya returned from the work with Prof. M. B. Ives at the McMaster University, Canada.

Our laboratory is mainly concerned with corrosion of metallic materials used in nuclear industries, Mössbauer spectroscopic study on corrosion of iron and steel, and hydrogen absorption in hydrogen reservoir alloys.

The subjects of these researches are listed as follow:

(1) Corrosion behavior of Hastelloy N in molten FLINAK salt.

(2) Polarization characteristics measurement of mild steel and austenitic stainless steels in various reagents for decontaminating the water coolant circuit of nuclear reactor.

(3) Characterization of very fine superparamagnetic α-FeOOH and α-Fe_2O_3, which seem to be important components of iron rust, by the Mössbauer spectroscopy and other methods.

(4) Lattic dynamic differentiation of Fe_3O_4 produced by air oxidation of iron and steel from the Mössbauer spectroscopic data.

(5) Retention behaviors of deuterium implanted in various metals with the $10 \sim 100$ keV Cockcroft-Walton accelerator.

(6) Prevention of pulverizing of non-stoichiometric Ti-Fe hydrogen reservoir alloy due to repeating hydrogenation and dehydrogenation.

Oral Presentation

Hydrogen Diffusion During Growth of Zirconium Hydride Layer; T. Mizuno, M. Nakai and T. Morozumi: The 17th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1982.

Potentiometric Analysis of Uranium; H. Ohashi, U. Watanabe and T. Morozumi: The 1981 Summer Meeting of the Hokkaido Sections of the Japan Chem. Soc. and the Japan Soc. for Anal. Chem., July., 1982.

Fine Structure and Hydrogen Reservoir Properties of Non-stoichiometric Iron-Titanium Alloys; T. Mizuno, T. Suzuki and T. Morozumi: *ibid.*, July 1982.

Super-paramagnetism Found in Iron Rust; T. Morozumi: Seminar of the corrosion of metals sponsored by the Hokkaido Corrosion Research Association, Aug., 1982.

ELECTROCHEMISTRY LABORATORY

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

Students

M. Masuda, K. Azumi, I. Shintani, H. Nagao,
T. Shimakura, Y. Kawamura, Y. Aoyama
and K. Inanaga

Current research in this laboratory may be divided into four groups : a) theoretical approach to metallic corrosion and passivation from thermodynamic and kinetic viewpoints, b) electron spectroscopic studies of the composition and structure of surface layers of passivated metals and alloys, c) ellipsometric and reflectometric studies of surface oxide films on metals, and d) electrochemical studies on the ion-selective and osmostic properties of corrosion precipitate films.

Research subjects in progress this year are as follows

(1) Thermodynamic and kinetic study of passivity breakdown and localized corrosion : Nucleation of film-breakdown sites due to anion-adsorption and stability of pit or crevice propagation are being studied theoretically by means of irreversible thermodynamics and mass transport kinetics.

(2) Enrichment and depletion of alloying elements in surface layers of iron-base alloys oxidized in aqueous and gases environments: There occurs enrichment or depletion of elements not only in the surface oxide but also in a surface layer of the substrate alloy.

(3) In-situ ellipsometric and reflectometric studies of the passive films on iron, nickel and titanium in acid and base aqueous solutions : Exact determination of the thickness and optical constants of the film is made and the light-absorption spectra are being measured for iron and nickel.

(4) Studies of the anodic oxidation and cathodic reduction of passive films on iron by means of a rotating ring-disc electrode.

(5) Anion-adsorption in hydrous iron and nickel oxide films anodically deposited on platinum.

(6) Mass and volume transport through corrosion precipitate membranes during anodic crevice corrosion: Anodic crevice corrosion causes anion-transport from the bulk solution to the crevice solution, which is accompanied by a volume flow leading to an increase of pressure in the crevice solution.

(7) Anodic oxidation of niobium in acid solution: The composition and defect structure of the anodic oxide film are being measured as functions of film-formation potential and solution composition.

(8) Formation of hydrous iron oxide precipitate films on aluminum-brass from soluble iron ions in sea water.

Prof. Sato visited Brazil from August 28 to September 6 as a member of a technical mission to observe the world-largest niobium deposit at Araxa and discussed with mining and metallurgical engineers there the potential use of niobium in advanced technology. He gave a lecture on metallic corrosion and passivation in the Technological Research Institute (IPT) in Saó Pauls on September 1. Prof. Sato also visited Soviet Union from October 10 to October 26 to attend the 3rd Japan-USSR Joint Corrosion Seminar held in Moscow and presented a lecture on the corrosion precipitate films on October 8. Prof. Sato and Dr. Seo participated in the JIMIS-3 (3rd Japan Institute Metals International Symposium) on High Temperature Corrosion of Metals and Alloys held on November 17-20 in Susono City, Japan, and presented a poster paper on selective oxidation of iron-nickel alloy.

Foreign visitors to this laboratory in 1982 are Dr. Vladimir Kazakov from the Institute of Physical Chemistry in Moscow on March 15-17, Prof. H. W. Pickering from the Pennsylvania State University in U. S. A. on May 10-12, Dr. V. A. Safonov from Moscow State University on July 21-22, Prof. Wayne L. Worrell from the University of Pennsylvania in U. S. A., Dr. G. Hultquist from the Royal Institute of Technology in Sweden on August 20-21, Dr. M. J. Graham from the National Research Council of Canada in Ottawa on November 22, Prof. Stanistaw Morovec from Poland on November 24, and Prof. K. N. Strafford from Newcastle Upon Tyne Polytechnic in G. B. on November 25.

Oral Presentation

Electrochemistry of Metal Surface; N. Sato: Hokkaido Section Aurora Seminar of Catalysis Soc. Japan, Jan., 1982.

Surface Stress of Metal Electrodes; M. Seo and N. Sato: Steel Branch Meeting of Hokkaido Section of JSUJ, Jan., 1982

Complex Refractive Index Spectrum of Anodic Oxide Film on Metals Measured by Refrectometry; T. Ohtsuka, K. Azumi and N. Sato: The 17th Hokkaido Section Meeting of Applied Physics Soc. Japan, Feb., 1982.

Study on Non-Stationary Dissolution of Passivated Iron by using Rotating Ring Disc Electrodes; I. Shintani, T Ohtsuka, and N. Sato: The 8th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1982.

Depth-concentration Profiles of Major and Minor Alloying Elements in Stainless Steels; M. Seo and N. Sato: The 17th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1982.

An AES Analysis of Passive Films on Iron-base Alloys in Concentrated Sodium Hydroxide Solution; Y. Sera, M. Seo and N. Sato: The Spring Meeting JIM, April, 1982.

Formation and Reduction of Anodic Oxides on HgTe and $Cd_{0.2}Hg_{0.8}Te$; H. -H. Strehblow, M. Sakashita and B. Lochel: International Conference on II–VI Group Compound Semiconductors (Durham), April, 1982.

Complex Refractive Index Spectrum of Surface Passive Film on Iron and Nickel; T. Ohtsuka, K. Azumi and N. Sato: The 49th Annual Meeting of Electrochem. Soc. of Japan, May, 1982.

Electrode Activity and Composition Change of Anodic Oxide Films on Tantalum Due to Vacuum-Heat Treatment; T. Sakon, M. Seo and N. Sato: *ibid.*, May, 1982.

Cathodic Reduction of Passivated Titanium; T. Ohtsuka, M. Masuda and N. Sato: '82 Spring Metting of the Japan Society of Corrosion Enginerring, May, 1982.

Selective Dissolution and Interdiffusion of Alloys; M. Seo and N. Sato: *ibid.*, May, 1982.

Depth-composition Profiles of Passive Films on Stainless Steels Containing Niobium; M. Seo, N. Sato and C. -G. Kin: *ibid.*, May, 1982.

Iron Oxide Film Formation on Al-Brass Condenser Tube; S. Ono, M. Sakashita, N. Sato and K. Okamoto: *ibid.*, May, 1982.

Hydrated Iron Oxide Precipitates and Crevice Corrosion —Ion Transport and Volume Flux—; T. Shimakura, M. Sakashita and N. Sato: The Spring Meeting of Hokkaido Section of JIM., May, 1982.

Selective Surface Oxidation Reaction of Fe–3ONi Alloys; M. Seo and N. Sato: '82 Hokkaido Section Summer Meeting of Japan Chem. Soc., July, 1982.

Stability of Passivation Film on Titanium under Cathodic Reduction in Acidic and Neutral Solutions; T. Ohtsuka, M. Masuda and N. Sato: The 5th Japan-USSR Seminar on Electrochemistry (Sapporo), Sept., 1982.

Depth-composition Profiles of Anodic Oxide Films on Niobium; M. Seo, F. Baba and N. Sato: The 91th Meeting of JIM., Sept., 1982.

Surface Treatment of HgTe and $Cd_{0.2}Hg_{0.8}Te$; M. Sakashita, H. -H. Strehblow and N. Sato: *ibid.*, Sept., 1982.

Potential Dependence of Surface Anodic Oxide Film of Nickel in Neutral Solutions; T. Ohtsuka, K. Azumi and N. Sato: *ibid.*, Sept., 1982.

Spectrum Measurement of Iron Passivation Films on Iron by 3-P Ellipsometry; K. Azumi, T. Ohtsuka and N. Sato: *ibid.*, 1982.

Role of Corrosion Precipitates in Passivation and Localized Corrosion of Metals; N. Sato and M. Sakashita: The 3rd USSR-Japan Seminar on Corrison (Moscow), Oct., 1982.

Selective Surface Oxidation of Fe-30Ni Alloy ; M. Seo and N. Sato : The 3rd JIM International Symposium on High Temperature Corrosion of Metals and Alloys (Susono), Nov., 1982.

ELECTROMETALLURGY LABORATORY

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

Students

S. Ohta, H. Tanaka, M. Okazaki, A. Kumatoritani
and Y. Shinno

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) A novel bipolar electrode cell, which we refer to as a rotating bipolar electrode stack cell, are developed to remove heavy metal ions from dilute solutions, and its fundamental functions are being investigated in a ferro-ferricyanide solution and in dilute cupric sulfate solutions.

(3) Evaluation of fifteen different organic corrosion inhibitors to prevent dezincification of α, β-brass was made using an electrochemical tecnhique, EPMA and atomic absorption spectroscopy. Heterocycric organic compounds, such as 2-mercaptobenzimidazole and benzotriazole, were found to be effective not only in onset of dezincification but also in controlling the dezincification layer growth.

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

Oral Presentation

A Modified Estimation Procedures of Operational Characteristics of Bipolar Electrode Cell for Electrowinning in Fused Salt; T. Ishikawa: The 8th Hokkaido Section Meeting of Electrochem. Soc. of Japan, Jan., 1982.

Composition of Volatile Species and their Temperature Dependencies from Chloride Melts Containing Aluminum Chloride; S. Ajimura, S. Konda and T. Ishikawa: *ibid.*, Jan., 1982.

Treatment of Cupric Sulfate Solutions with Rotating Electrode Stack Cell under Various Electrolytic Conditions; K. Orita, T. Sasaki and T. Ishikawa: *ibid.*, Jan., 1982.

Bnzotriazole and Tolyltriazole as Corrosion Inhibitors for Aluminum Alloys; T. Notoya and T. Ishikawa: The 17th Annual Meeting of the Hokkaido Corrosion Research Association, Jan., 1982.

Corrosion Inhibition of Aluminum Alloys by Benzotriazole and its Derivatives; T. Notoya and T. Ishikawa: The 1982 Winter Meeting of the Hokkaido Section of the Japan Chemical Society, Feb., 1982.

Estimation of Operational Characteristics and Design Rules of Bipolar Electrode Cell; T. Ishikawa and S. Konda: The Meeting on Chemical Energy, Grant-in-Aid for Energy Research, The Ministry of Education, Science and Culture, Feb., 1982.

Use of Benzotriazole and its Derivatives as Corrosion Inhibitors for Copper Alloys in Fresh Water; T. Notoya: The 4th Meeting of Corrosion Research Group on Copper Alloys, March, 1982.

Inhibitive Effect of Benzotriazole and its Derivatives on Aluminum Alloys in Hydrochloric Acid Solutions; T. Notoya and T. Ishikawa: The 45th Annual Meeting of Japan Chemical Society, April, 1982.

Corrosion Inhibitors for Alminum Alloys: Benzotriazole and Tolyltriazole; T. Notoya and T. Ishikawa: '82 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1982.

Inhibition Action of Benzotriazole Derivatives on Corrosion of Aluminum Alloys; T. Notoya and T. Ishikawa: The Hokkaido Section Meeting of JIM., May, 1982.

Determination of Diffusion Limiting Current Density in Rotating Bipolar Electrode Stack Cell; T. Sasaki, M. Chida and T. Ishikawa: The 49th Annual Meeting of the Electrochem. Soc., of Japan, May, 1982.

Calculation of Metal Layer Thickness on the Electrodes by Analysis of Operational Characteristics of Bipolar Electrode Cell; M. Okazaki, S. Konda and T. Ishikawa: *ibid.*, May, 1982.

Electrowinning of Aluminum from Chloride Melts; T. Ishikawa: *ibid.*, May, 1982.

Development of Electrolytic Process of Aluminum from Chloride Melts for Energy Saving; T. Ishikawa: The Meeting on Chemical Energy, Grant-in-Aid for Energy Research, The Ministry of Education, Science and Culture, Aug., 1982.

Electrochemical Treatment of Cupric Sulfate Solution with Rotating Bipolar Electrode Cell (Part 3) Scale-up of the Cell; T. Sasaki and T. Ishikawa: The 1982 Fall Meeting of the Electrochem., Soc., of Japan, Oct., 1982.

Electrowinning of Liquid Aluminum by using Funnel-Pile Type Bipolar Electrode Cell (Part 10) Design Rule for Bipolar Electrode Cell; T. Ishikawa and S. Konda: The 16th Symposium on Molten Salt Chemistry, Nov., 1982.

Development of Alminum Electrowinning Process with Chloride and Bipolar Electrode Cell (Part 1) Performance of Rectangular Bipolar Electrode Cell; M. Okadera, M. Okazaki, S. Konda and T. Ishikawa: *ibid.*, Nov., 1982.

Atmospheric Corrosion Testing in Japan

T. Fukushima, N. Sato, Y. Hisamatsu,
T. Matsushima and Y. Aoyama

"Atmospheric Corrosion" Ed. by W. H. Ailor, John
Wiley & Sons Inc. 1982, pp. 841~872

This paper describes the experimental procedures and results of atmospheric exposure tests of metals and alloys in various environments in Japan. Scientific studies of atmospheric corrosion products are also introduced, and the mechanisms of corrosion resistance of weathering steels are reviewed. Artificial rust studies, which simulate the atmospheric corrosion, have provided relevant information on the reactivity of hydrous metal oxides which constitute the initial product of atmospheric corrosion. Also reviewed are atmospheric corrosion monitroing techniques and accelerated atmospheric corrosion tests. (English)

The Stability of Pitting Dissolution of Metals in Aqueous Solution

N. Sato

J. Electrochem. Soc., **129**, No. 2, 260 (1982)

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

Measurements of the Corrosion Rate of Iron in Aqueous Solution by Means of A Square Wave Current Polarization with Compensation of Solution Resistance

T. Ohtsuka and N. Sato

Corrosion Engineering (Boshoku Gijutsu),
31, No. 5, 336 (1982)

The corrosion rate of pure iron in aqueous solutions has been examined by a square wave linear polarization method as functions of solution pH, amount of oxygen dissolved in solution, and salt concentration. A square wave current with the pulse width of $\Delta t=$ 30s (frequency $f=0.017$ Hz) was adopted to measure the apparent polarization resistance, R_p+R_s, and it was interrupted for a short time less than 0.1 ms at an interval of 1 ms to estimate the solution resistance R_s. From the polarization resistance R_p the corrosion current i_c of iron was estimated within 15% error in sulphate solutions in a wide range of pH from acid to alkali by using the following equation, $i_c=K/R_p$ with $K=0.025$ (V). In sulphate solutions of 0.5 mol $\mathrm{kg}^{-1}[\mathrm{SO}_4^{2-}]$ under the air-opened condition, the corrosion current of iron decreases with pH in acidic solutions ($\mathrm{pH}<4$), whereas in neutral solutions ($4<\mathrm{pH}<10$) the corrosion current is independent of pH. In alkaline solutions ($\mathrm{pH}>10$) iron becomes passivated. Both salt concentration and dissolved oxygen concentration in sodium sulphate solution influence the corrosion current. With increasing concentration of sodium sulphate, the corrosion rate decreases in aerated and oxygenated solutions but it increases in deaerated solutions. (Japanese)

Introductory Remark to High Temperature Water Corrosion of Iron Base Alloys

N. Sato

"Predictive Methods for Assessing Corrosion Damage
to BWR Piping and PWR Steam Generators"
Ed. by H. Okada and R. W. Staehle,
NACE, 1982, pp 320~324

This article reviews a few fundamental concepts which are of importance in understanding the high temperature water corrosion of iron-base alloys. Firstly, the thermodynamic stability of iron and other alloying metals is illustrated in the potential/pH diagram, which is the basic standpoint of corrosion investigation. Secondly, the two apparently different corrosion mechanisms that are expected to operate on the metal surface in high temperature water are described; they are the electrochemical corrosion and the chemical corrosion. The third concept is the localization of corrosion which usually results from either local acidification or basification of environmental solution at particular places on the metal surface determined by thermal-hydraulic conditions, solid deposits, and non-homogeneous surface composition of alloys. Finally, the effects of the metallurgical condition on corrosion are briefly discussed. (English)

Surface Composition and Corrosion of SS 41 Carbon Steel in High Temperature Water under γ-ray Irradiation

A. Sakumoto, M. Gotoda, Y. Horii, H. Konno,
H. Tamura and M. Nagayama

Corrosion Engineering, **31**, 254 (1982)

The effect of γ-ray irradiation on the corrosion of SS 41 carbon steel in high temperature water was studied. The average corrosion rate was measured after 48 or 96 hr exposure to distilled water containing different DO ($5\sim700$ ppb) at 250°C. The amount of Fe ions in the film and that dissolved in water were separately determined by weight measurement combined with a film dissolution technique. The composition of oxide films was determined by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction. After 48 hr the corrosion rate with γ-ray irradiation was larger than that without irradiation, whereas after 96 hr no detectable difference was observed. By X-ray diffraction the bulk composition of the oxide film was found to be mainly magnetite. XPS showed that γ-ray irradiation forms unknown oxygen compounds, OX, other than O^{2-} and OH^-, and also graphite-like substance on the surface. The intensity of the carbon spectra was three to four times higher when γ-rays were irradiated. It is considered that the mechanism of corrosion under γ-ray irradiation is different from that without γ-ray. The corrosion rate and the surface composition showed no clear relationship with DO in the range examined in this work. It is interesting to note, however, that the average dissolution rate of Fe increases with the amount of OH^- (without γ-rays) or OX (with γ-rays) on the oxide surface. (Japanese)

Benzotriazole and its Derivatives as Corrosion Inhibitors for Iron in Sodium Chloride Solutions

Takenori Notoya and Tatsuo Ishikawa

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110 p. 119 (1982)

Inhibitive effect of benzotriazole (BTA), tolyltriazole (TTA) and benzotriazole carboxylic acid (BTA-COOH) on the corrosion of iron was investigated in the inhibitor concentration range of 10^{-5} to 10^{-3} mol/l in aerated 3% sodium chloride solutions at 50°C by weight loss measurements using a spinner test assembly and electrochemical techniques. The corrosion test results indicate that the inhibition efficiencies increases with the increasing inhibitor concentration and the effectiveness increases in the order of TTA (inhibition efficiency 18.7%)<BTA (26.5%)<BTA-COOH (34.9%) at the concentration of 10^{-4} mol/l. At the concentration of 10^{-3} mol/l, however, the inhibition efficiency of BTA-COOH remains almost constant because of its solubility limit in the solution while those of TTA and BTA were 57 and 63%, respectively. The potentiostatic polarization curves of iron show that the inhibitors increase both anodic and cathodic polarization and inhibition of the cathodic reaction, mainly oxygen reduction reaction, is more pronounced than that of anodic one. Relationship between the degree of potential change ΔE and the inhibitor concentration C suggests that the inhibition action may be attributed to Langmuir-type adsorption of the organic molecules at cathodic sites on the iron electrode. (English)

Recent Applications of Benzotriazole and Its Derivatives

T. Notoya

Rust Prevention and Control, Vol. 26,
No. 3, March, 10 (1982)

Among the corrosion inhibitors for copper and copper base alloys, benzotriazole and its derivatives generally rank as the most effective and have been widely used in various environments for about 30 years. Efforts are still being made to improve their effectiveness and to extend their application. A review is given of the recent applications of benzotriazole and tolyltriazole mainly as inhibitors for cooling water systems, antifreeze and engine coolants, solar energy systems, coating materials, lubricants, greeses, dielectric oils, cleaning solvents, anti-tarnishing ditergents, fire hydrant systems. Corrosion inhibition mechanisms of the inhibitors are also described. (Japanese)

Anodic Breakdown of Passive Films on Metals

N. Sato

J. Electrochem. Soc., **129,** No. 2, 255 (1982)

The electrocapillary stability of passive films on metals has been studied in terms of energetics. It is predicted that there is a critical potential above which breakthrough pores are formed in the film. This critical film breakdown potential is less noble, as the surface tension at the metal-electrolyte interface is smaller and hence as the anion adsorption is stronger. It is also predicted from the dissolution kinetics of semiconducting surface films that above a certain critical potential the passive film is electrochemically unstable, undergoing potential-dependent transpassive dissolution. Anion adsorption, which introduces electron acceptor levels in the film, will lower the transpassivation potential at the adsorption sites. The passive film of n-type oxide appears to be more stable against anodic polarization than that of p-type oxide. (English)

Depth Analysis of Passive Films on Iron in Neutral Solution

N. Sato, K. Kudo and R. Nishimura

Proceedings of The 6th Intern. Congr. Met.
Corr., Vol. 1, p 301 (1975)

An electrochemical depth profiling of passive films has been employed by means of cathodic reduction combined with ellipsometry and chemical analysis. The results indicate that the film formed in neutral solution is bilayered with a barrier layer of iron oxide, which changes from ferric-ferrous mixed oxide to ferric oxide as the potential is raised, and a deposit layer of ferric hydroxide, which remains nearly unchanged in an extended range of potential. There is a concentration peak of either excess irons or iron ion vacancies at the barrier-deposit boundary in the film and the excess iron ions are gradually replaced by iron ion vaxancies as the potential is more noble. The thickness of the barrier layer for unit voltage is 1.54 nm/V at less noble potentials and 1.75 nm/V at more noble potentials. It is the barrier layer alone that increases in thickness during the steady growth of the film. Transpassivation causes the barrier layer to cease growing with potential and generates a small concentration of ferrous ions in the layers. (English)

Advantages of Pulse Anodizing

K. Yokoyama, H. Konno, H. Takahashi
and M. Nagayama

Plating and Surface Finishing, No. 6, 62 (1982)

By pulsing the potential during anodizing, anodic films on aluminum can be improved. Pulsing from a high to a lower voltage (e. g., 22 to 15 V) increases corrosion and abrasion resistance considerably, improves thickness uniformity and reduces the total time required to produce a given thickness. Using pulse anodizing, hard coatings can be made thicker with less energy for solution chilling. (English)

The Hydration of Barrier Oxide Films on Aluminium and Its Inhibition by Chromate and Phosphate Ions

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

Corrosion Science, **22**, 913 (1982)

Compact oxide films were formed on aluminium in a neutral borate solution (pH 7.4, 20°C) by applying a constant potential of 50 V (SCE), and then immersed in distilled water, a 0.001 mol dm^{-3} chromate solution (pH 7.0), or a 0.001 mol dm^{-3} phosphate solution (pH 7.0). Changes in the composition profile of the oxide caused by the immersion were examined by X-ray photoelectron spectroscopy (XPS) combined with a film sectioning technique. After a 72 hr immersion in distilled water, the OH^- content in the outer part of the film increased to about three times as that before immersion, and the film sustained only 30 V instead of the initial 50 V. As the profile of BO_2^- ions remained unchanged, the deterioration of the film is exclusively due to hydration of the oxide caused by the penetration of water molecules or OH^- ions into the oxide lattice. It was found that the hydration is strongly inhibited by chromate and phosphate. XPS and chemical analysis showed that CrO_4^{2-} and PO_4^{3-} ions adsorb on the oxide surface to form a mono- or bi-layer, hindering the penetration of water molecules. The inhibiting behaviour, stabilizing oxide films, is important in explaining the function of these anions as corrosion inhibitors for metals in near neutral solutions. (English)

Effects of Electrolyte Anions on the Formation of Barrier Type Oxide Films on Aluminum

H. Takahashi, Y. Saito and M. Nagayama

J. Metal Finish. Soc. Japan, **33**, 522 (1982)

Aluminum was anodically oxidized to form barrier type oxide films at 5.0 A/m^2 and 20°C in adipate, borate, citrate, oxalate, phosphate, and tartrate solutions of $pH=7$ at different concentrations between 10^{-3} and 1.0 M. From measurements of the rate of increase in anode potential, dE_a/dt_a, and dissolution rate of Al^{3+} ions, dW_d/dt_a, the oxide formation current i_f, oxide dissolution current, i_d, and electronic current, i_e, were determined as a function of electrolyte concentration. It was found that with increasing concentration, i_f reaches a maximum between 10^{-2} and 10^{-1} M after which it decreases considerably, and i_d reaches a minimum in the same concentration range. The oxide formation current, i_f, in the 10^{-1} M solutions decreases in the following order. Adipate > Phosphate > Citrate > Tartrate > Oxalate > Borate. The electronic current, i_e, is appreciable at 10^{-3} M, while it is negligibly small at concentrations higher than 10^{-2} M. The role of the electrolyte anions on the formation of barrier type oxide films is discussed in terms of the pH-buffering ability and complexing ability of the electrolyte anions. (Japanese)

Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water

I. Effect of film thickness and reaction time on the degree of hydration and acid-dissolution characteristics

M. Koda, H. Takahashi and M. Nagayama

J. Metal Finish. Soc. Japan, **33**, 242 (1982)

Porous oxide films anodically formed on Al at a constant c. d. in an oxalic acid solution were immersed in hot water at 99.5°C and time-variation in the degree of hydration was followed by weight measurements. The oxide films were then dissolved in a chromic acid-phosphoric acid solution to measure the weight loss-time characteristics. The results of the experiments were analyzed as function of the initial film thickness (or anodizing time) and the time of hot water treatment. Conclusions we obtained regarding the hydration and dissolution behavior are as follows: 1) In initial periods, the hydration proceeds at the entire pore-wall surface leading to a decrease in pore diameter. The density of the formed hydrous oxides is estimated to be 2.5～2.7, while that of the original oxide is around 2.9. The rate of hydration decreases as the hydrous oxides fill up the pores; this is more pronounced for thicker films. 2) For the oxide films hydrated for a very short time ($t_h < 3$ min) the dissolution occurres in a way to widen the pores so that the time required to dissolve out the oxide does not depend on the initial film thickness. When the pores are filled up with the hydrous oxides, the dissolution proceeds at a considerably slower rate because of a decrease in the area of the surface exposed to the acid solution. Thus, the time needed to dissolve out the film increases as the initial film thickness increases. After prolonged hot water treatment ($t_h > 30$ min), the outmost part of the hydrous oxide becomes very resistant to acid dissolution. (Japanese)

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

K. Ebihara, H. Takahashi and M. Nagayama

J. Metal Finish. Soc. Japan, **33**, 156 (1982)

Electropolished 99.99% Al foil coupons were anodized in H_2SO_4 solutions of $0.5\sim4.0\ \mathrm{mol\cdot dm^{-3}}$ at $10\sim40°C$, by applying a constant current in a range of $0.5\sim50\ \mathrm{mA\cdot cm^{-2}}$. Morphology of the oxide films was examined using electronmicroscopic and electrochemical techniques. For the accurate estimation of the number of pores, N, from electronmicrographs, the pores were widened by chemical dissolution of the oxide in a H_2SO_4 solution before the film was stripped from the substrate metal. The total film thickness, h, was estimated from the sections of films under a scanning electron-microscope, and the pore radius, r, was calculated from the porosity of the oxide, α $(=N\pi r^2)$, measured by the pore-filling method proposed by Middelhoek. The estimation of the barrier layer thickness, δ_b, was made according to Hunter's principle by measureing the voltage jump, E_j, when applying a small anodic current in a neutral borate solution. The thickness/voltage ratio, δ/E_j, was determined from the time-variations in the pore-wall thickness, δ_p, and E_j during chemical dissolution of the oxide, on an assumption that δ_b and δ_p thin at equal rates. In agreement with the results reported previously, N decrease and r and δ_b increase as the anodizing voltage, E_a, increases, but the results of this investigation clearly show that these quantities are solely the function of E_a although E_a is strongly affected by the solution condition and anodizing c. d. It is demonstrated that δ_b/E_a ratio is not constant but decreases with increasing E_a. For films formed with a fixed number of coulombs, the value of h somewhat increases with increasing E_a, solution concentration and temperature. The density of oxide ρ, is estimated to be 3.0-3.5 by dividing the weight of the film by the oxide volume calculated from the values of h, N, r and the

chemical dissolution rate of the pore-wall during anodizing. It is interesting ntoote that ρ decreases with increasing E_a, solution concentration and temperature. The significance of the techniques of determining the quantities describing the film structure is discussed. (Japanese)

Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water

II. Analysis of Film Structure by Impedance Measurements

M. Kohda, H. Takahashi and M. Nagayama

J. Metal Finish. Soc. Japan, **33**, 614 (1982)

Porous oxide films with different thicknesses were formed on aluminum at a constant c. d. of 10 mA/cm^2 in an oxialic acid solution. They were treated with hot water at 99.5°C, and the time-variation in the film structure due to hydration was followed by impedance measurements in a boric acid-borate solution. The frequency range examined was 0.1–10,000 Hz and the results were analyzed using a Bode diagram method in which the log of the absolute value of impedance was plotted against the log of the frequency. The equivalent circuit of the hydrated film was found to consist of the capacitance, C_b, of the barrier oxide layer, combined in series with a parallel combination of the capacitance and resistance components, C_h, and R_h, of the hydrated oxide in the pores. The values of these components were determined using the fact that C_b, R_h, and C_h are decisively responsible for the film impedance in the frequency range of $<10, 10\sim500$, and $500\sim10{,}000$ Hz, respectively. For films thicker than 0.8 μm (or anodizing time $t_a>3$ min), $1/C_b$, initially 6 $\mu F^{-1}\cdot$cm^2, decreases with the hydration time, t_h, and reaches a steady value of about 4.5 $\mu F^{-1}\cdot$cm^2 at $t_h=10\sim20$ min. This indicates that the barrier layer thickness decreases with t_h due to hydration occuring from the outside and that the hydration reaction becomes extremely slow when the pores are filled up with hydrous oxide at time beyond $t_h=10\sim20$ min. The $1/C_h$ value, corresponding to the thickness of the hydrous oxide phase increases with t_h for $10\sim20$ min to reach a steady value which is roughly propotional to the initial film thickness. The value of R_h is roughly propotional to t_a at any t_h but it continues to increase with t_h even after $1/C_h$ becomes steady, suggesting that

the specific resistance of the formed hydrous oxide increases with time by an aging effect. For thin films formed for $t_a = 1$ min, oxide is completely hydrated within $t_h = 20$ min and thereafter the substrate metal gradually reacts with hot water. These findings are in agreement with the results of previous investigation, in which the weight gain of the films due to hydration was examined. (Japanese)

Anodic Oxide Films and Electrochemical Reactions on HgTe

M. Sakashita, H. -H. Strehblow and M. Bettini

J. Electrochem. Soc., **129,** No. 4, 739 (1982)

Anodic oxidation processes on HgTe surfaces in acetate buffer pH4.9, borate buffer pH 8.4, and 0.1 M KOH pH 13.0, with and without ethylene glycol, have been studied. Pt-split ring-HgTe-disk electrode experiments permit the simultaneous examination of formation and reduction of oxides and of soluble reaction products. The composition and thickness of the anodic oxide layers are evaluated coulometrically. XPS measurements yeild the chemical composition of the HgTe surface after the different electrochemical treatments. They essentially confirm the electrochemical analysis. Optically homogeneous oxide layers of up to ~1000 Å thickness are grown in acetate buffer, borate buffer, and 0.1 M KOH–90% ethylene glycol. The layers are composed of mixed oxides, $TeO_2 \cdot xHgO$, with $x<1$. The molar ratio HgO/TeO_2 levels off to a value of $x \simeq 0.5$ for high oxidation potentials in acetate buffer and reaches almost $x \simeq 1.0$ for the KOH-ethylene glycol micture. The missing Hg is dissolved as $Hg(OH)_2$ during anodic oxidation with only a small amount of Te compounds. The first cathodic reduction step of the oxides in the same electrolytes reduces HgO to metallic Hg. As a consequence TeO_2 is dissolved, demonstrating the importance of the HgO for the chemical stability of the mixed oxide layer. Special cathodic reduction conditions ($-0.6\ V_H$ in acetate buffer) produce a stoichiometrically clean HgTe surface, removing any oxide or elemental Te at the surface due to previous chemical treatments. The electrochemical reactions are similar for all three electrolytes mentioned above. However, in pure 0.1 M KOH the disk and ring currents are more than one order of magnitude larger ($<1\ mA\ cm^{-2}$) than those in acetate and boric borate buffer ($\sim 0.1\ mA\ cm^{-2}$,)

indicating a higher dissolution rate of these oxide layers. The presence of 90% ethylene glycol in 0.1 M KOH reduces the current density again to the low levels (<0.1 mA cm^{-2}). (English)

Anodic Oxide Films and Electrochemical Reactions on $Cd_{0.2}Hg_{0.8}Te$

M. Sakashita, H. -H. Strehblow and M. Bettini

J. Electrochem. Soc., **129**, No. 8, 1710 (1982)

The formation and reduction of anodic oxide on $Cd_{0.2}Hg_{0.8}Te$ (CMT) are studied by electrochemical methods and x-ray photoelectron spectroscopy (XPS). The anodic oxide is formed at $\varepsilon >$ 0.8 V for pH 4.9 and $\varepsilon > 0.6$ V for pH 13 (SHE). The CdO and HgO contents relative to TeO_2 increase within the oxide with the pH value. In a small potential range, $\varepsilon = 0.6 \sim 0.8$ V, pH 4.9, and $\varepsilon = 0.3 \sim 0.6$ V, pH 13, CdTe is oxidized separately. This behavior leads to a CdO-rich oxide surface layer in alkaline solutions whereas in acidic solutions the CdTe oxidation products are dissolved completely and the oxide is stabilized only by an HgO content for $\varepsilon > 0.8$ V. In alkaline solutions, CMT shows a small Cd deficiency at the semiconductor-oxide interface according to an increased Cd content for the oxide. Ethylene glycol is a necessary additive to 0.1 M KOH to form a well-pasivating film presumably by the reduction of the solubility of the oxide. The presence of Cd and Hg in the bulk and CdO and HgO within the oxide is a necessary condition from the side of the solid phase. The formation of tellurites and ditellurites seems reasonable to explain the stability of the passivating oxide layer. (English)

An Examination of the Electrode Reactions of Te, HgTe and $Cd_{0.2}Hg_{0.8}Te$ with Rotating-Split-Ring-Disc Electrodes

M. Sakashita, B. Lochel and H. -H. Strehblow

J. Electroanal. Chem., **140**, 75 (1982)

Te, HgTe and $Cd_{0.2}Hg_{0.8}Te$ (CMT) have been examined with the rotating-ring-disc technique. The oxidation and reduction of these materials as well as of the anodic oxides have been studied in solutions of pH 1 to 13. The soluble oxidation products of four-valuent Te and two-valent Hg may be determined quantitatively at a Pt-ring. Hg metal deposits at the disc are seen by the additional formation of soluble monovalent Hg^+-ions during oxidation. Passivating oxides are formed on HgTe and CMT in weakly acidic or alkaline solutions (pH 4.9, 8.4) or in 0.1 M KOH in 90% ethylene and 10% water. From the characteristics of the reduction of the anodic oxide it is deduced that a compound oxide rather than an oxide mixture is present. The HgO- and CdO-content reduce significantly the dissolution of TeO_2 presumably by the formation of tellurites. At sufficiently positive potentials ($E \approx 0$ V) only the HgO-content may be reduced to Hg. At more negative values (-0.3 V) HgTe and Te are formed. The reduction of HgTe and CMT leads to Cd- and Hg-metal deposits and soluble telluride. (English)

High Temperature Corrosion of Heat-Resisting Alloys

K. Nishida

Bull. Japan Inst. Met., **21**, No. 9, 696 (1982)

This review paper gives an outline of the recent investigations on high-temperature corrosion of heat-resisting alloys. The subjects in this review are as follows:

(1) Classification of heat-resisting alloys
(2) Apporach to the problem of high-temperature corrosion
(3) High-temperature corrosion in various atmospheres
(4) Scale morphologies
(5) Protection against high-temperature corrosion
(6) Trend of recent investigation
(7) Theme to be expected in future (Japanese)

CRGHU

High Temperature Sulfidation of Chromium

—Kinetics and Scale Structures—

T. Narita and K. Nishida

Report of the 123rd Committee on Heat Resisting Metals
and Alloys, Japan Society for the Promotion
of Science, **23**, No. 2, 241 (1982)

Sulfidation behavior of chromium was investigated over the wide range of sulfur partial pressures, $10^{3.8}-10^{-6}$ Pa, in H_2S-H_2 atmospheres at temperatures of 973, 1073 and 1173 K by using of TGM, X-ray diffraction, optical microscopy, SEM and EPMA. In general, an initial linear scale growth was followed by a parabolic scaling. The external scale formed on chromium consists of the multi-layers: $[Cr_2S_3(rh)/Cr_2S_3(tri)/Cr_3S_4/CrS_x]$, $[Cr_2S_3(tri)/Cr_3S_4/CrS_x]$, $[Cr_3S_4/CrS_x]$, $[Cr_7S_8+Cr_{15}S_{16}]$, or $[CrS_x]$, depending upon sulfur partial pressures. The sulfur concentrations and phases of chromium sulfides formed on the metal were good agreement with the phase diagram proposed by Rau, except for the mixed phases of $[Cr_7S_8+Cr_{15}S_{16}]$ and the single phase of [CrS]. It was suggested that the CrS_x phase had high diffusivity of Cr. Thus, the addition of Cr to alloys is not effective to enhance sulfidation resistance in low sulfur partial pressures. (Japanese)

The High Temperature Corrosion of Some Fe–Al Alloys under Low SO_2 Partial Pressures

K. Kurokawa, T. Narita and K. Nishida

Corrosion Engineering (Boshoku Gijutsu),
31, No. 3, 133 (1982)

The corrosion of some Fe–Al alloys containing up to 7 mass% Al at 1073 K under SO_2 partial pressure below 10^3 Pa was studied by thermogravimetry, X-ray diffraction, SEM, and EPMA. The effect of pre-oxidation on the corrosion of the alloys was also clarified. The addition of aluminum yielded a significant improvement in the corrosion resistance of the alloys to SO_2 gas. The parabolic rate constants obtained at given SO_2 partial pressures were exponentially decreased with the aluminum content, which was due to the increasing depression of the sulfide formation in the external scale. The increased corrosion resistance was interconnected to the depressed formation of sulfide for the alloys with high aluminum content, because of the reduced transport rate of cations through the oxide scale. The pre-oxidation treatment for the alloys yielded the remarkable decrease of the corrosion rate and the sulfide in the scales was scarcely found during the subsequent corrosion in the SO_2 atmospheres. (Japanese)

High Temperature Corrosion of Metals and Alloys in Sulfur-Containing Atmospheres

K. Kurokawa, T. Narita and K. Nishida

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110, 187 (1982)

In order to clarify the mechanism of simultaneous oxide and sulfide formation in metals and alloys at high temperatures in sulfur-containing atmospheres, the corrosion of iron and chromium in SO_2 atmospheres was studied by thermogravimetry, X-ray diffraction, SEM-EDAX, optical microscopy, EPMA and Auger electron spectroscopy. The scale formed on iron at 1073 K consisted of iron oxides (FeO, Fe_3O_4) and sulfide (FeS), while only chromium oxide (Cr_2O_3) was formed on chromium at 1273 K in any SO_2 atmosphere. Especially, the iron oxides and sulfide showed the lamellar structure only in low SO_2 partial pressures where the sulfur partial pressure was lower than the dissociation pressure of FeS.

The formation of the lamellar structure on iron is explained by a rapid consumption of oxygen causing the sulfide formation, as a result of a local rise in the activity of the sulfur adsorbed on the scale surface, and the fluctuations in the adsorbed oxygen and sulfur activities. Thus, in order to control of the sulfide formation, the following methods were attempted.

(1) The increase of oxygen potential in atmosphere.

(2) The formation of a scale having a low cation diffusivity with some Fe-Cr alloys.

Finally, the latter exhibited a more remarkable control of the sulfide formation than in the former. (Japanese)

Some Aspects on the Preferential Sulfidation at the Grain Boundary of Fe-Cr Alloys

T. Narita and K. Nishida

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110, 199 (1982)

Grain boundary sulfidation, which is often observed beneath the surface scales on the heat-resistant alloys, is discussed on the basis of theoretical calculation and sulfidation experiments of the Fe-Cr alloys in H_2S-H_2 atmospheres. When the Fe-medium Cr alloys were sulfidized at sulfur pressure lower than the dissociation pressure of a ferrous sulfide, the preferential sulfidation along the grain boundaries emerged from below the thin surface scale. Diffusional analyses were made to simulate the sulfide growth and chromium depleted zone after considering thermodynamical limitations peculiar to sulfidation at very low sulfur pressures. A good agreement was obtained between the calculated and measured values, except for the parabolic rate constants k_p of the Fe-medium Cr alloys sulfidized below a critical sulfur pressure. In these alloys the measured values for k_p were much larger than the calculated ones so that the preferential sulfidation at the grain boundaries may explain the difference between the two.

Two necessary conditions are proposed for the preferential attack at the grain boundary:

(1) The diffusion flux of the sulfide phase is higher than that of an alloy phase.

(2) The concentrations of less-noble metals in the sulfide phase are larger than the alloy compositions. (Japanese)

The Influence of Oxygen Pressures on the Oxidation Behavior of a Co-0.45 mass%Ni Alloy at Elevated Temperatures

T. Narita, K. Kimura and K. Nishida

J. Japan Inst. Met., **46**, No. 8, 792 (1982)

A Co-0.45 mass%Ni alloy oxidizes parabolically by formation of a (Co, Ni)O scale when exposed in the oxygen pressure range from 2.6×10^2 to 10^5 Pa at temperatures of 1373, 1473 and 1573 K. The nickel gradient within the scale decreased with increasing outward distance due to nickel migrating slowly than cobalt, which profiles tended to be flattened with decreasing oxygen pressures and elevating temperatures.

A computer simulation is made for the scale growth on the alloy and a cobalt metal. Computation demonstrates that agreement between the calculated and experimental determinations of the parabolic rate constants k_p was good, but not very good for dependences of values for k_p and concentration profiles upon the ambient oxygen pressures.

It was found at temperature of 1473 K that the oxygen activities $(1.5\sim4.1\times10^{-3})$ shifted toward higher values than the equilibrium value of 2.9×10^{-5} at the oxide/alloy interface enable the calculated values for k_p and concentration profiles to coincide with the observed ones. These results could be ascribed to the formation of fine pores and micro-cracks in the vicinity of the scale/alloy inteerface. The analogous oxidation behavior might be expected to see for the scale growth on a pure cobalt metal. (Japanese)

Metallic Materials Against Sulphur Attack

K. Nishida

Kinou Zairyo, 1.2, No. 8, 8 (1982)

High-temperature sulfidation of metallic materials is very important in the current industries. This review paper gives an outline of the sulfidation behaviors of metals and alloys, especially iron and iron based alloys. It was suggested that the addition or coating of elements such as Al, Si and Cr to alloys were effective to enhance sulfidation resistance. (Japanese)

Computer Simulation of the Diffusional Growth of Ternary Oxides Scales on Binary Alloys

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

J. Electrochem. Soc., **129,** No. 1, 209 (1982)

A computer solution is made of the equations for growth by ambipolar diffusion of metal of the ternary monoxide scales on Co-Fe and Co-Ni alloys. Computations demonstrate that the parabolic scaling rates and the compositional profiles in these scales calculated using independently obtained diffusional and thermodynamic properties of the solid phases in the alloy-oxide systems are in agreement with the experimental determinations. Results are analyzed for oxidation of Co-Fe containing up to 10 a/o Fe to (CoFe)O at 1473 K in oxygen at $10 \leq P_{O_2} \leq 10^5$ Pa and the oxidation of Co-Ni alloys containing up to 7 a/o Ni to (CoNi)O at 1373, 1473, and 1573 K in oxygen at 10^5 Pa. (English)

Improvement of Oxidation Resistance of Ta Metal Sheets by Means of Metallizing of Their Surface

K. Nishida

Research Report of Workshop on First Wall Coating,
Institute of Plasma Physics, Nagoya Univ.,
IPPJ-551, 192 (1982)

In order to improve the oxidation resistance of refractory metals, the diffusion coating on the Ta metal sheets by siliconizing, chromizing and calorizing were investigated.

In general, the growth of the diffusion layer of these coatings obeyed parabolic rate laws. The siliconized, chromized and calorized alloy layers consisted of $TaSi_2$, $TaCr_2$ and $TaAl_3$, respectively.

The oxidation resistance of the chromized Ta sheet is better than that of the siliconozed one. However, the chromized alloy layer is very fragile, so that the siliconized layer is more preferable.

The oxidation behavior of the calorized Ta sheets was somewhat different from previous ones. It is concluded that the most effective compound to keep a significant oxidation resistance seems to be the $TaA10_4$ double oxide which is easily formable and stable at 1373 K.

In this report, the effect of preoxidation on the oxidation resistance of the calorized Ta sheets and the oxidation behaviors of other calorized refractory metals such as Mo and Zr are also discussed. (English)

Sulfidation Properties of Fe–Cr Alloys at 1073 K in H_2S–H_2 Atmospheres of Sulfur Pressures 10^{-2} and 10^{-5} Pa

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

Oxidation of Metals, **17**, Nos. 5/6, 299 (1982)

An investigation is reported on the sulfidation properties of Fe–Cr alloys over their complete compositional range in H_2S–H_2 atmospheres at 1073 K. Sulfidation of alloys containing less than 60 at.% Cr obeyed parabolic kinetics and alloys of larger chromium content and chromium followed linear kinetics. Scales were composed of two distinct layers : an outer columnar grained sulfide and an inner equiaxed grained sulfide layer of increased relative thickness and porosity at larger alloy chromium contents. The scales on quenched specimens were composed of either $(CrFe)_5S_6$ or (FeCr)S plus small amounts of $(FeCr)_3S_4$ at $P_{S_2}=10^{-2}$ Pa and of $(CrFe)_5S_6$ at $P_{S_2}=10^{-5}$ Pa. Internal sulfidation was most pronounced in the high chromium content alloys and at the low sulfur pressure. The parabolic sulfidation rate at $P_{S_2}=10^{-2}$ Pa was large and of practically constant value irrespective of alloy composition. These kinetics at $P_{S_2}=10^{-5}$ Pa, however, increased from a very low value by three orders of magnitude as the alloy chromium content was increased from 5∼60 at.%. (English)

Spectroscopic-Ellipsometric Studies of Surface Passivation Films on Metals

T. Ohtsuka, K. Azumi and N. Sato

Reports of the Asahi Glass Foundation for
Industrial Technology, **41**, 197 (1982)

For iron the spectra of the complex refractive index of the passivasion film resemble that of α-Fe_2O_3. The light absorption edge, i. e., bandgap, of the film appears at about 2.0 eV whose value is fairly close to that of Fe_2O_3. It is therefore likely that the film is mainly composed of Fe_2O_3. The solution pH influences the thickness and refractive index of the film. With decreasing pH value the film thickness decreases and the refractive index increases. This influence of pH value may be explained by the hydration of the film, which depends on the solution pH.

For nickel it was found that the transition from passivation to transpassivation occurs at potential of $E=1.2$ V (vs Hydrogen Electrode at the Same Solution ; HESS) in pH 8.4 borate solution. At potentials more negative than this potential nickel is covered with a very thin oxide layer of 0.9 nm thickness having a refractive index of 2.0 – 2.5. In the potential region more positive than 1.2 V the anodic oxide film becomes thick and its refractive index changes to $n=1.35-1.40$, which corresponds to that nickelic hydroxide $NiOOH \cdot H_2O$.

For titanium the refractive index of the passivation film, $n=2.1$, is smaller than that of bulk TiO_2 and the light absorption edge, $E_{BG}=3.2$ eV, estimated from the extinction index is comparable to that of TiO_2. It is conceivable that the passivation film is composed of partially hydrated TiO_2. (Japanese)

Measurements of High Temperature Oxidation Rates of Iron by Mössbauer Spectroscopy

T. Morozumi, M. Otsuka and H. Ohashi

Corrosion Engineering (Boshoku Gijitsu), **31**, 226 (1982)

Oxidation of iron has been studied in air at temperatures from 450 to 600°C by in situ measurements of Mössbauer absorption spectra combined with thermogravimetry and scanning electron microscopy. The oxidation proceeded in two succesive stages from α-Fe to Fe_3O_4 and to α-Fe_2O_3. The first stage of oxidation was well expressed by a first order rate law and the second stage by a parabolic rate law. The first stage of oxidation was attributed to a two-dimensional, heterogeneous growth of Fe_3O_4 on the iron surface and the second stage to diffusion controlled process. The activation energies were 46.6 for the first stage and 48.4 kcal/mol for the second stage. Thermogravimetric results were shown to follow the same rate laws obtained by Mössbauer spectroscopy. Observation by scanning electron microscope supported the interpretations. Mössbauer spectroscopy showed that the total iron contained in the detected constituents decreased with the increase in measuring temperature. This was determined to be due to the temperature dependence of the Mössbauer absorption intensity being higher for the oxidized Fe_3O_4 than for bulk Fe_3O_4. These observations are ascribed to the marked difference in the force constant, or the Debye temperature, between both kinds of Fe_3O_4. (Japanese)

Film Growth and Depth-Composition Profiles of Surface Oxides on Fe-30Ni Alloy

M. Seo and N. Sato

J. Surf. Sci. Soc. Japan, **3**, No. 1, 11 (1982)

Fe-30Ni alloy samples were oxidized for 10 to 240 minutes at 433 to 473 K under a pure oxygen pressure of 1.33×10^4 Pa. The thickness of oxide films was measured by a multiple-angle 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 the iron component is preferentially oxidized, producing a nickel-enrichment zone in the alloy side of the film/alloy interface.

As the oxidation time or the oxidation temperature increases, the nickel-enrichment zone thickens, whereas the concentration gradient in the nickel-enrichment zone decreases. During oxidation of the alloy, the rate of transport of iron component in the film was almost equal to the interdiffusion rate in the substrate alloy, indicating a steady-state. The apparent value of interdiffusion coefficient, $\bar{D}$ estimated at the steady-state is $7.3 \times 10^{-16}\,\mathrm{cm^2 \cdot s^{-1}}$ at 473 K, which is more than ten orders of magnitude higher than the value extrapolated from the lattice-diffusion data obtained at high temperature. The large value of $\bar{D}$ may be explained in terms of the divacancy-enhanced lattice diffusion mechanism rather than the grain boundary diffusion mechanism. (Japanese)

Interdiffusion in the -Solid Solution of the Co–Zn System

T. Yamamoto, T. Takashima and K. Nishida

Memoirs of the Hokkaido Institute of Technology,
No. 10, 1 (1982)

For the purpose of studying interdiffusion in the α-solid solution of the Co–Zn system, the experiments were performed using a method of vapor-solid couple at temperature between 1173 K and 1373 K.

Fine alumina markers placed on the test pieces prior to diffusion remained on the surface after annealing.

The interdiffusion coefficients ($\tilde{D}$) were dependent upon Zn concentration and were evaluated to be the orders of $10^{-16} \sim 10^{-13}$ m^2/s in this experimental temperature range.

The activation energies for interdiffusion ($\tilde{Q}$) decreased from 284 to 221 kJ/mol with increasing Zn concentration.

The impurity diffusion coefficients of Zn in Co, D^*_{Zn} between 1273 and 1373 K were obtained from extraporation of $\tilde{D}$ to 0 at%Zn and its activation energy, Q^*_{Zn}, was evaluated to be 297 kJ/mol. (Japanese)

Influences of Test Piece Profile and Dimension on the Tensile Strength of Flake Graphite Cast Iron

T. Noguchi and K. Nagaoka

IMONO, 54, 3 (1982) 145

Variation in the measured strength of gray iron resulting from the differences in the profile and dimension of test pieces was examined. Experiments were performed on the test pieces with various fillet radii, gauge lengths and section diameters. Results were analyzed theoretically utilizing the stress distribution obtained by finite element method, and the stress-strain curves of each test piece. Fillet radius does not have any effect on the strength of cast iron unless it is too small in comparison to the section diameter. This is because the stress around fillet relaxes with the non-elastic behavior of cast iron. The length and diameter of the test section affect the strength in different ways. That is, the strength obviously decreases with increase in diameter, while it is not affected or slightly increased by increasing of diameter. Consequently, the statistical theory where the strength decreases with increasing specimen volume can not be applied to cast iron. The phenomenon in cast iron is explained by the fact that the eutectic cell structures of graphite flakes at the surface layer act as defects and result in the reduction of the net sectional area of the specimen. This effect becomes more pronounced in small specimens. (Japanese)

Strength Evaluation of Cast Iron Circular Plate by the Finite Element Method

T. Noguchi and K. Nagaoka

AFS Transactions 82-64 (1982) 323

From experiments, the nominal bending strength of cast iron components computed from conventional formulas is 2 to 3 times the tensile strength. This is attributed to non-elastic properties of the material. In this study, the finite element method was used to analyze the mechanical behavior and bending strength of circular plates, and a new method is proposed for evaluating strengths under a wide range of nonuniform stresses.

The evaluation of fracture strength proposed for cast iron circular plate is two steps. First elastoplastic stress calculation by strain incremental theory with FEM is made to obtain the stress distribution in the plate. Here, the non-linear stress-strain relation in tension and compression were approximated by numerical functions. The results showed that the maximum stress in the plate exceeded the tensile strength, although it was remarkably lower than the elastic stress. The second step is the application of a facture criterion considering the contrast between calculated stress and fracture strength obtained from tensile test. The criterion is also valid for beams, plates, and tension of notched bars, etc.

In practice, the fracture strength of cast iron components under a stress gradient is defined by a overstressed depth δ at which the stress analyzed by FEM coincides with tensile strength of the iron. The value of δ is 2 to 4 mm at room temperature, and decreases to about 1 mm at very low temperature or under steep stress gradients. Metallurgically, the minimum size, or unit, of overstressed depth δ is understood to be the size of the graphite eutectic cell, which may be the unit of microstructural fracture in cast iron. (English)

Changes of Graphite Phase in Grown S. G. Iron

K. Nagaoka and M. Sōma

NIRECO NEWS, 17 (1982) Oct. 32

Quantitative analysis of graphite phase by Q. T. M. of LUZEX 450 was applied on grown S. G. iron with various size of graphite nodules. The results were explained according to a growth mechanism proposed by the authors and gave metallurgical evidence to the thesis.

The analysis by LUZEX 450 was used particularly to examine the redistribution of graphite nodules followed by the growth, since the mechanism proposed is based on the irreversible migration of graphite during heating and cooling. Changes of fractional area of graphite phase and numbers of graphite nodules in the microstruture due to carbon migration between graphite and matrix were quantified well and the increase of both corresponded to the growth of the iron.

Growth properties of S. G. iron depended significantly on the nodule size and the growth rate of coarse graphite iron was about twice as large as the rate of fine graphite iron. In the coarse iron the number of graphite increased remarkably and fine nodules had generated, though in the fine graphite iron graphite nodules were enlarged as large as 1.5 times of the initial size. These results are mainly attributed to the distance of carbon diffusion in the matrix during heating and cooling. (Japanese)

Observation of Spheroidal Graphite Cast Iron Grown in Air by Scanning Electron Microscope and XMA Analyser

M. Sōma and K. Nagaoka

IMONO, 54, 12 (1982) 795

The purpose of the present work is to clarify and consider in detail the effect of oxidation on the growth of spheroidal graphite cast iron by investigating the whole structure up to 10% linear growth in air. (1) The diameter of the iron decreased gradually due to the formation and loss of the oxide scale by repeated heating between room temperature and 950°C in air. (2) The grown iron has a four layer structure: the outer layer is composed of pure iron oxides; the second layer, ferrite; the third, pearlite, and the central area is composed of pearlite and ferrite. Eacg layer increased in its thickness with the progress of repeated heating except the central part. (3) In the primary growth stage of the iron, the oxidizing atmosphere formed only a slight oxide and decarburization layer. But the atmosphere gradually penetrate into the inside starting from 4% linear growth. (4) As the supply of oxygen became samller from external atmosphere to the third layer, the stmosphere formed with the reaction of porous graphite nodules turned carburizing rather than oxidizing and denser pearlite was formed due to the carburizing phenomenon during cyclic heating. (5) No effect of oxidation was observed in the central area of the iron even after 10% linear growth. A metallurgical behavior was shown on the dilatometric curves. Furthermore, the tensile strength retained was 43.5 kgf/mm^2 compared to 55.6 kgf/mm^2 of the as-cast iron. This may be attributed to the effect of carburizing atmosphere fromed in the third layer. (6) Except for the extreme outer layer, redistribution of graphite and diffusion porosity due to graphite migration were observed by the scanning electron microscope but the spheroidal graphite nodule in the outer layer affected strongly by the external atmosphere lost its shape and the internal surface of the cavity became smoother. (Japanese)

Thermochemical Decomposition of H_2S with Nickel Sulfide

H. Kiuchi, K. Funaki, Y. Nakai and T. Tanaka

Proceedings of the 4th World Hydrogen Energy
Conference, Vol. 2, 543-551, (1982)

The two-step thermochemical decomposition cycle of H_2S was proposed as described below and the experimental studies were made on the cycle.

$$\begin{array}{l} Ni_3S_2 + H_2S = 3NiS + H_2 \\ 3NiS = Ni_3S_2 + S \\ \hline H_2S = H_2 + S \end{array}$$

The use of lower sulfide such as Ni_3S_2 was regarded as rather important based on thermodynamic and kinetic investigations.

Ni_3S_2 power was mixed with Al_2O_3 to avoid the sintering being associated with the depression of melting point caused by desulfurization of NiS. In the fundamental experiments, the effects of reaction factors were investigated. The cycle under optimum conditions was scaled up by 10 times and the thermal efficiency was estimated to be 51～54%. (English)

Thermochemical Decomposition Cycle of H_2S with Metal Sulfides

H. Kiuchi and T. Tanaka

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110, 1-11, (1982)

In thermal decomposition of H_2S, the equilibrium H_2 concentration is a mere only 7 vol-% at 800°C. In order to improve this low decomposition, a two-step process was studied by combining sulfurization of metal sulfide at about 500°C and thermal decomposition of the sulfurization product at 800°C under reduced pressure. Ni_3S_2 powder was mixed out of necessity and dispersed in inert powder (Al_2O_3 or MoS_2) or other metal sulfide (FeS or Cr_2S_3) because of its easy sintering. Mixing of an inert powder prevented the sintering and provided a stationary high decomposition rate of H_2S. The average H_2 concentration was about 60 vol-%. The mixture with FeS caused the formation of pentlandite and the cycle gave a somewhat lower yield of hydrogen than that with the inert powder mixture. Though the mixture with Cr_2S_3 formed also a double sulfide, it gave about 60 vol-% of the average H_2 concentration. In addition, the sulfurization at such low temperatures as 300°C was possible because the sulfurization rate was enhanced. The thermal efficiency was estimated to be 52～55% for the cycle with the mixture of Al_2O_3 and Ni_3S_2. This high value implies that the production of H_2 from H_2S may be practical. (Japanese)

Thermochemical Splitting Cycle of H_2S with Ferrous Sulfide

—Recovery of H_2 and S° from H_2S 1st Report—

H. Kiuchi, T. Iwasaki and T. Tanaka

Journal of the Mining and Metallurgical Institute
of Japan, Vol. 98, No. 1132, 523-528, (1982)

This cycle consists of a combination of sulfurization of ferrous sulfide with hydrogen sulfide and thermal decomposition of the sulfurization product under normal or reduced pressure.

Three types of ferrous sulfide, thermal decomposition product of natural pyrite, natural pyrrhotite, and synthetic ferrous sulfide were examined.

Both sulfurization product and thermal decomposition product in every cases were identified as ferrous sulfide by X-ray diffraction analysis. But the formation of higher sulfide such as pyrite in sulfurization is not always desirable, because it gives thermodynamically very small hydrogen concentration. A representation for the two step process in this research can therfore be given in the following equations, provided that FeS_{1+x} and FeS_{1+x+y} indicate nonstoichiometric composition of the sulfide.

$$\begin{array}{l} FeS_{1+x} + yH_2S = FeS_{1+x+y} + yH_2 \\ FeS_{1+x+y} = FeS_{1+x} + yS \\ \hline yH_2S = yH_2 + yS \end{array}$$

The thermal decomposition product of natural pyrite showed the most favorable results for obtaining not only higher concentration of hydrogen but also larger amount of evolved hydrogen. This may be due to the porous solid structure caused by the volume contraction under thermal decomposition.

In the cyclic experiments, the hydrogen concentration at the sulfurization increased with an increase in the decomposition temperature, whereas the temperature determined as optimum for sulfurization was in the range from 500 to 650°C. The latter result can be considered as resulting from the interplay of the temperature dependence of the reaction rate and the equilibrium concentration of hydrogen. (Japanese)

Recovery of Hydrogen from Hydrogen Sulfide with Metals or Metal Sulfides

H. Kiuchi, T. Nakamura, K. Funaki and T. Tanaka
Int. J. Hydrogen Energy
Vol. 7, No. 6, 477-482, (1982)

The following two types of reaction were investigated for the recovery of hydrogen from hydrogen sulfide :

Type 1 reaction (M : metal)

$$(M \text{ or } M_xS_y) + zH_2S = (MS_z \text{ or } M_xS_{y+z}) + zH_2$$
$$(MS_z \text{ or } M_xS_{y+z}) = (M \text{ or } M_xS_y) + zS^\circ$$

$$zH_2S = zH_2 + zS^\circ$$

Type 2 reaction (M : metal)

$$M + zH_2S = MS_z + zH_2$$
$$MS_z + zO_2 = M + zSO_2$$

$$zH_2S + zO_2 = zH_2 + zSO_2$$

Each type of reaction is constructed by a two-step cycle, in which H_2S is reacted with metal or metal sulfide and then the resulting sulfide undergoes thermal decomposition or oxidation. Ag_2S, FeS, Co_9S_8, Ni_3S_2, and the double sulfide $CuFeS_2$ were examined in the former type or reaction, while Ag, Cu, Ni, liquid Pb, and liquid Bi-Ag alloy were used as an intermediate in the latter. (English)

Partial Desulfurization of Copper Concentrates with Hydrogen and Copper Enrichment by Hydrochloric Acid Leaching

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University, No. 110, 13 (1982)

The activated leaching of chalcopyrite with hydrogen was investigated in this paper for the up-grading of concentrates and the recovery of S as S^0 and of as Fe_3O_4. Desulfurization of copper concentrates with hydrogen was found to be most effective as compared to thermal decomposition under reduced pressure or in an inert gas stream. The reaction proceeds as shown below: $CuFeS_2 \rightarrow \beta$-chalcopyrite→bornite$+Fe_{1-x}S \rightarrow Fe+$bornite$\rightarrow Fe+Cu$.

Coagulation of the deposited FeS into a massive particle and formation of bornite phase surrounding it were observed under a light microscope. Also, it was found that partially reduced products were leached readily by hydrochloric acid solution with a vigorous evolution of H_2S and then Cu_2S was formed. The dissolution of iron in bornite was affected significantly by nonstoichiometry of bornite and was slightly influenced on the acid concentration or leaching temperature. (Japanese)

Electrowinning of Liquid Aluminum From Chloride Melts by Using a Bipolar Electrode Cell

T. Ishikawa and S. Konda

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110, 107 (1982)

Experimental studies on electrowinning of liquid aluminum from aluminum chloride melts using bipolar electrode cells have been carried out for several years in our laboratry in order to develop a new process for energy saving.

This paper describes the outline of this research and development courses including cell design, construction of electrolytic apparatus and operational techniques.

Typical data on recent electrolysis are as follows. Funnel-type of graphite bipolar electrode 10 unit cell, electrolyte: NaCl–$MgCl_2$ (3:1) containing few % $AlCl_3$, temperature: 750°C±10°C, applied current to end electrodes: 70 A (ca. 1 A/cm^2), cell efficiency: 88~90%, net electrolysis duration: 5 hours, average bath voltage per unit cell: 2.6~2.8 V, aluminum produced: 876 g, purity: 99.98%, electrolytic energy demand: about 10,000 kw•hr/ton-Al.

It was also found for further saving of energy that concentration of aluminum chloride in the melt should be maintained at the lowest level possible desirably, below 3 mol.% during electrolysis. (Japanese)

Application of Rotating Bipolar Electrode Stack Cell to Electrolysis of Dilute Cupric Sulfate Solution

T. Sasaki, K. Orita and T. Ishikawa

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110, 125 (1982)

A novel bipolar electrode cell, which we refer to as a rotating bipolar electrode stack cell, was developed for electrolytic recovery of heavy metals from very dilute solutions. The cell consists of the stack of two feeder electrodes and nine bipolar electrodes which are rotated at every other electrode. The solution is helically flowed through the inter-electrode gaps passing through the peripheries of rotors and the center holes of stators.

An electrolyte containing 100 ppm Cu^{2+} ions was continuously pumped externally and/or by a self-pumping action through the cell from a well mixed reservoir and the variation in cupric ion concentration in the course of electrolysis was investigated under various conditions of rotational frequencies, volumetric flow rates and electrolytic currents.

It was found that the mass transfer rate was markedly promoted by the rotation and the concentration differences between at inlet and at outlet of the cell were lowered under the high volumetric flow rate, and this results in an increase in the metal recovery rate and current efficiency. Under the electrolytic condition of 200 mA, 1400 r.p.m. and 3.4 $l\,\mathrm{min}^{-1}$ the concentration of 30 l solution changes from 100 ppm to 10 ppm for 98 minutes and simultaneously the current efficiency reaches about 70%. (Japanese)

Titanium Concentration in $FeTi_x$ ($1 \leqq x \leqq 2$) Alloys and its Effect on Hydrogen Storage Properties

T. Mizuno and T. Morozumi

Journal of the Less-Common Metals, 84, 237 (1982)

The effect of the surface and bulk properties of $FeTi_x$ ($1 \leqq x \leqq 2$) on its hydrogen storage characteristics was investigated by X-ray photoelectron spectroscopy, Mössbauer spectroscopy and metallographic observations. It is shown that several problems encountered with FeTi, such as the necessity of employing activation treatment and the surface sensitivity resulting form poisoning by impurity gases, can be reduced if alloys with a non-equilibrium structure are prepared by the addition of excess titanium. (English)

Removal of Arsenic from the Waste Hot-Water from GeothermalPower Plants

Tadao Nagai, Rintaro Togashi and Masanori Yamaguchi

Bull. Fac. Engr. Hokkaido Univ., No. 110 (1982)

Removal of arsenic by means of ion-exchange technique was studied for the treatment of waste hot-water from geothernal power plants, in order to utilize the thermal energy for multi-purpose use. An inorganic ion-exchanger, hydrated zirconium oxide, was used in both the column adsorption and the two-stage counter-current adsorption techniques.

A specially designed ion-exchanger was used in the former technique, i. e., the hydrated zirconium oxide was dispersed on a granular porous carrier. Although some loss of the hydrated zirconium oxide from the carrier occurred during repeated experiments, no arsenic was found in the effluent until the break-through point and a significant improvement on the adsorption kinetics was observed in comparison with some commercial exchangers.

In the latter technique, the hydrated zirconium oxide powder, made by the Freeze-Melt process, was used for its adequate particle size for solid-liquid separation at the thickener. The results obtained were sufficient to pass the Government's regulation tests (<0.5 ppm), but insufficient for some local regulation tests (<0.05 ppm). Since the operations and maintenance are simple and also the assurance for the arsenic level in the effluent stream can be easily given, the latter technique seems to be practical, while some improvement are still required to pass the local regulation tests. (Japanese)

Removal and Recovery of TBP in a Raffinate by Carbon Tetrachloride-Scrubbing

Gaku Kano, Rintaro Togashi and Tadao Nagai

Proc. Symp. Solvent Extraction 1982,
Hamamatsu (Dec. 1982)

A single stage scrubbing using CCl_4 was found to be an efficient technique in order to eliminate the solvent loss to raffinate streams from SX. Experimental results are shown in the case of SX of As^{5+} from copper electrolyte using 100% TBP. Recovery of CCl_4 by reduced pressure distillation from bleeded CCl_4 was successfully made, resulting 1 : 1 mixture of TBP and CCl_4. (English)

Removal of Chelating Agents and Heavy Metal Ions from Laboratory Wastewaters

S. Emi, H. Tamura and M. Nagayama

J. Metal Finishing Soc. Japan, **33**, 291 (1982)

In Hokkaido University, laboratory wastewaters are collected periodically, and treated in a treatment plant. Usually, the collected wastewaters are very acidic and contain various heavy metal ions as well as chelating agents. The precipitation of heavy metal ions as hydroxides will be incomplete unless the chelating agents are pretreated by oxidation. A special treatment process in which CrO_3, Fe^{3+}, and Ca^{2+} are added prior to the neutralization with NaOH solution has been adopted to overcome this difficulty. This paper describes the basic research conducted to develop the treatment process, especially in relation to the oxidation of chelating agents by CrO_3. Among many chelating agents, EDTA, DTPA, and Tetren strongly interfere with the formation of metal hydroxides. However, EDTA and DTPA are easily decomposed by CrO_3. The effectiveness of CrO_3 addition is demonstrated for (A) an actual wastewater to which some EDTA had been added, and (B) a number of model wastewater containing Fe^{3+}, Zn^{2+}, Cr^{3+} ions, EDTA, and other chelating agents. The proper operating conditions for oxidation, i. e., CrO_3 concentration, solution acidity, temperature, and reacting time are determined experimentally. (Japanese)

Study on Ceramic to Metal Bondings —Part 1—

Application of the Cu-O Filler to the Al_2O_3-Ni Bondings

T. Narita, K. Sugawara and K. Nishida

Bulletin of the Faculty of Engineering, Hokkaido
University, No. 110, 177 (1982)

Alumina to nickel bondings were developed using the copper oxygen alloys as a filler in an inert gas atmosphere at temperatures between 1338 to 1356 K. Copper and three alloys containing (A) hypo-, (B) hyper-, and (C) hyper rich in Cu_2O-eutectic compositions were used and the optimum bonding time was determined with a cathetometer, which allows for the determination of the onset of melting down the alloy fillers.

Numerous voids were found in the vicinity of the Al_2O_3/Cu-O alloy interface and their sizes tended to be smaller than those of the bonding heated in air. These viods seem to be attributable to the stress relief during cooling.

The three-point bending test was adopted at room temperature to reveal that welldabilities of copper and alloys increased in the sequence of copper, alloys of C, A, and B. The bonding made with the alloy B was fractured along the grain boundaries within the Al_2O_3 phase. It was found that the large specimen had a fracture strength higher than that of the small one, because the so-called notch effect became significant for the small specimen.

The good adhesiveness of the Cu-O alloy B could be interrelated to the lower contact angles of the molten alloys to the alumina surface, i. e., to the highly established wettability. (Japanese)

Precipitation of Cobalt Ferrites

H. Tamura and E. Matijević

J. Colloid and Interface Sci., **90**, 100 (1982)

Cobalt ferrites were prepared by againg at 90°C either (A) coprecipitated iron (II) and cobalt (II) hydroxides from aqueous solutions of $Co(NO_3)_2$ and $FeSO_4$, or (B) ferrous hydroxide gels in contact with Co (II) salt solutions. In both case KNO_3 was added to act as a mild oxidizing agent. Magnetic particles were formed when the equivalent concentration of metal ions exceeded that of the hydroxide ion. The chemical composition and the morphology of particles varied with the concentrations of the reacting components in the original solutions. Under certain conditions spherical particles of narrow size distributions were obtained. (English)