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

Professor T. Ishikawa, Electrometallurgy Laboratory,
Professor N. Sato, Electrochemistry Laboratory,
Professor T. Morozumi, Nuclear Reactor Materials Laboratory

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

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Mr. Y. Umehara, Mr. Z. Zhu, Mr. N. Katayama
and Miss S. Akiyama

Students

M. Mitsuta, I. Saeki, S. Shibahara
and M. Itoh

Professor Nagayama received the Takei Prize from the Electrochemical Society of Japan for "Electrochemical Study on the Surface Finishing of Metals" in April, 1985. In May he was invited to the American Electrochemical Society Meeting at Toronto to give a lecture. He was a chairman of the organizing committee of the 32nd Annual Symposium on Corrosion and Protection, which was held at Hokkaido University in August. In October Mr. Otake was awarded a prize by the Japan Society for Analytical Chemistry for his many years of services in chemical analysis work.

Mr. Zhu Zufang from General Research Institute for Nonferrous Metals, Beijing (China), stayed in our laboratory from January to December, 1985. Mr. N. Katayama from the Asahikawa Technical College joined our group in May. Mr. Umehara returned to Nippon Gakki Seizo Co. in August.

Dr. Takahashi made a presentation at the Japan-US Corrosion Seminar at Nikko in March. Dr. Tamura joined the 5th International Conference on Colloid and Surface Science at Potsdam (N. Y., U. S. A.) in June. In September Prof. Nagayama, Dr. Tamura, and Mr. Katayama went to Graz (Austria) to present papers at the 2nd Battery Material Symposium, and Prof. Nagayama further attended the International Electrochemical Society Meeting at Salamanca (Spain).

Two foreign scientists visited our laboratory: Prof. H. Leidheiser, Jr. from Lehigh University, Bethlehem (Penn., U. S. A.), in March, and Prof. J. L. Leach from Nottingham University, Nottingham (England), in November.

The research projects completed or in progress at our laboratory are :

(1) Formation and deterioration of composite oxide films on aluminum.

Composite oxide films were formed by anodizing aluminum covered with a hydrous oxide, and were examined by electrochemical measurements and electron microscopy. The composite oxide was found to consist of two layers : an inner amorphous oxide layer and outer crystalline oxide layer. The crystalline oxide layer contained 'voids' which causes a deterioration of oxide on open circuit in water. The deterioration was correlated with the distribution of voids in the oxide.

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

Cu-Al and Si-Al alloys were anodized in a sulfuric acid solution to form porous oxide films. The structure and formation behavior of the oxide film were examined as functions of the content of alloy element (Cu or Si) and anodizing condition.

(3) Effect of surface pretreatments on the high temperature oxidation of type 430 stainless steel.

Various surface pretreatments were applied on the stainless steel (16 Cr steel) to give different chromium content in the surface layer. The surface composition was determined by XPS. The treated steel samples were oxidized at 1100°C in air containing 0.2 atm water vapor. The effect of surface treatments on the oxidation behavior was examined by a gravimetry.

(4) High temperature oxidation of Fe-Cr alloys in an atmosphere containing water vapor.

Type 430 stainless steel (16 Cr steel) and Fe-Cr alloys having different Cr content (–30 mass%) were oxidized at 900-1100°C in the atmosphere where oxygen pressure was kept constant at 0.17

atm but water vapor pressure was varied from 0.2 atm to 0.03 atm. The effect of water vapor on the oxidation was followed by a gravimetry. The project is still in progress.

(5) Surface modification of zinc as a means for corrosion protection.

Zinc was immersed or anodized in a neutral solution containing small amount of organic compounds. Several compounds were found to modify zinc surfaces to be resistant to corrosion in chloride media. Compositions and protective abilities of the produced surfaces were examined.

(6) Adsorption of Zn^{2+} ions on MnO_2.

Adsorption of Zn^{2+} ions on MnO_2 samples was examined as a function of solution pH and Zn^{2+} ion concentration. The amount of adsorbed Zn^{2+} increased with the pH and the Zn^{2+} concentration in solution. The behavior was described with a Frumkin type isotherm in which retardation of adsorption due to electrostatic repulsion or steric hindrance of adsorbed Zn^{2+} is taken into consideration. The isotherm contains an equilibrium constant and a constant for the retardation effect. The values of the constants clearly reflected the different properties of oxide prepared under different conditions.

(7) Acid-Base dissociation of surface hydroxyl groups on metal oxides.

Surface hydroxyl groups on metal oxides release H^+ and OH^- ions to solution (acid-base dissociation), forming positive and negative sites. The difference in the amounts of these charged sites is the surface charge. In this investigation the surface charge was measured by acid-base titration for manganese dioxide and magnetite as functions of pH and the concentration of (1–1) electrolyte (sodium nitrate). The charge is positive at lower pH, and becomes negative after pzc (point of zero charge). With increasing concentration of the electrolyte, the slope of charge-pH curve increases, and pzc moves slightly towards lower pH. The results can quantitatively be explained by considering the equilibrium condition of the surface dissociation.

(8) Dissolution of magnetite in EDTA solutions

Magnetite particles were dissolved at 80°C for 9 h in deaerated EDTA solutions with different pH, and the saturated concentration of dissolved iron was measured. In the absence of EDTA the dissolution proceeds only below pH 2. With EDTA there is dissolution up to pH 8. Two distinct pH regions were observed, from pH 2 to 4, the concentration of dissolved iron reaches 1.5 times that of EDTA, and from 5 to 7, the iron concentration becomes equal to the EDTA concentration. The dissolution involves the following processes: (1) transfer of Fe^{2+} and Fe^{3+} ions from magnetite to the solution, and (2) chelation of the dissolved Fe^{2+} and Fe^{3+} ions with EDTA (H_4Y) to form $Fe^{II}Y$ and $Fe^{III}Y$. The solubility product of magnetite was estimated to be $19\,mol^{-5}m^{15}$, and the concentration of dissolved iron was calculated as the sum of the equibibrium concentrations of the species, i. e., Fe^{2+}, Fe^{3+}, $Fe^{II}Y$, and Fe^{III} Y. The calculations well explain the dissolution behavior.

Oral Presentation

Corrosion Behavior and Corrosion Potential of Carbon Steel in High Temperature Water; K. Mabuchi, H. Takahashi and M. Nagayama: The 11th Hokkaido Section Meeting of the Electrochemical Society of Japan, Jan. 1985.

Effect of Water Vapor on the Oxidation of Type 430 Stainless Steel at 1100°C; T. Shigekuni, H. Konno and M. Nagayama: The 20th Annual Meeting of the Hokkaido Corrosion Research Association, Jan. 1985

Ion Exchange Reactions on MnO_2 Surfaces; M. Mitsuta, H. Tamura and M. Nagayama: The 1985 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb. 1985.

Adsorption of Co^{2+} Ions on magnetite and the formation of Co-ferrites; H. Tamura: The 15th Meeting of the Water Chemistry Research Committee, Feb. 1985.

Effects of Oxygen Concentration on the Corrosion Behavior of Carbon Steel in High Temperature Water; K. Mabuchi, Y.

Horii, H. Konno, H. Takahashi and M. Nagayama : U. S. A.-Japan Seminar for Reducing the Corrosion of Steels, Nikko (Japan), Feb. 1985.

Formation of Hydrous Oxide Films on Aluminum in Hot Amine-Containing Solutions ; N. Sato, H. Takahashi and M. Nagayama : The 71st Annual Meeting of the Metal Finishing Society of Japan, Mar. 1985.

Equilibria of Ion-Exchange Reactions at Surface Hydroxyl groups on Manganese Dioxide —Effect of pH and Electrolyte concentration— ; H. Tamura, M. Mitsuta and M. Nagayama : The 50th Spring Annual Meeting of the Japan Chemical Society, Apr. 1985.

Anodizing of Aluminum Covered with Hydrous Oxide ; H. Takahashi, Y. Umehara and M. Nagayama : Annual Meeting of Electrochemical Society, Toronto (Canada), May. 1985.

Effect of Water Vapor on the High Temperature Oxidation of Type 430 Stainless Steel ; H. Konno, T. Shigekuni and M. Nagayama : JSCE '85, May, 1985.

Characterization of MnO_2 by Zn^{2+} Ion Adsorption ; H. Tamura and M. Nagayama : 5th International Conference on Surface and Colloid Science, Potsdam (N. Y., U. S. A.), June. 1985.

Ion-Exchange Behavior of Several MnO_2 Samples ; M. Mitsuta, H. Tamura and M. Nagayama : The 1985 Summer Meeting of the Hokkaido Sections of the Japan Chemical Society and the Japan Society for Analytical Chemistry, July. 1985.

Decrease in Zn^{2+} Ion Adsorptivity of MnO_2 by Heat Treatment ; N. Katayama, T. Nakai, H. Tamura and M. Nagayama : *ibid.*

Dehydration and Crystalization of Hydrous Oxide Films on Aluminum by the Influence of Anodic Field ; H. Takahashi, Y. Umehara and M. Nagayama : The 1985 Summer Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan. July. 1985.

Electrochemical Consideration on the Acid-Base Equilibria at Metal Oxide/Solution Interfaces ; H. Tamura and M. Nagayama : The 32nd Symposium on Corrosion and Protection, Aug. 1985.

Effects of Temperature on the Formation of Composite Oxide Films on Aluminum ; H. Takahashi, Y. Umehara and M. Nagayama : The 32nd Annual Symposium on Corrosion and Protection, Aug. 1985.

Electrochemical Measurements of Corrosion Rates of Carbon Steel in High Temperature Water ; K. Mabuchi, H. Takahashi and M. Nagayama : *ibid.*

Effect of Pretreatments on the High Temperature Oxidation of Type 430 Stainless Steel in a Moist Atmosphere ; I. Saeki, T. Shigekuni, H. Konno and M. Nagayama : The 32nd annual Symposium on Corrosion and Protection, Aug. 1985

Acid-Base Dissociation of Surface Hydroxyl Groups on Manganese Dioxide in Sodium Nitrate Solutions ; H. Tamura, M. Mitsuta and M. Nagayama : The 2nd Battery Material Symposium, Graz (Austria), Sept. 1985.

Adsorption of Zn^{2+} Ions on MnO_2 with and without Heat Treatment ; H. Tamura, N. Katayama, T. Nakai and M. Nagayama : *ibid.*

Accurate Characterization of Surface Oxide Films on Aluminum ; H. Takahashi : "Ryokuin" Seminar Sponsored by the Hokkaido Section of the Japan Society for Analytical Chemistry, Sep. 1985.

Hot-Water Hydration of Porous Anodic Oxide Films on Aluminum — Analysis of Film Structure by Anodic Polarizations ; M. Koda, H. Takahashi and M. Nagayama : The 36th ISE Meeting, Salamanca (Spain), Sep. 1985.

Acid-Base and Ion-Exchange Properties of Magnetite Surfaces ; H. Tamura, S. Shibahara and M. Nagayama : The 34th Annual Meeting of the Japan Society for Analytical Chemistry, Oct. 1985.

Dissolution behavior of Magnetite in Acid Solutions Containing Chelating Agents ; H. Tamura, M. Nagayama and S. Takasaki : The 72nd Annual Meeting of the Metal Finishing Society of Japan, Oct. 1985.

Chemical and Electrochemical Treatments of Zinc as a Means for

Improving Corrosion Resistance; Zufang Zhu, H. Konno and M. Nagayama: The 72nd Annual Meeting of the Metal Finishing Society of Japan, Oct. 1985.

ELECTROMETALLURGY LABORATORY

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

Students

K. Nishimura, R. Hatazawa, T. Horie, H. Kimura,
J. Koishikawa, A. Sato, K. Miura and H. Mizuno

Researches 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) Sulfidation-oxidation behaviors of boiler tubes in atomospheres encountered at oil fired boilers.

(3) The ceramic-metal bonding: bonding of Si_3N_4 and stainless steel with Ni–Ti filler and improvement of bonding layer by diffusion treatments.

(4) Studies on prevention of brasses from dezincification attack with heterocyclic organic inhibitors in chloride containing solutions and effect of phytic acid on anodic behavior of copper and its alloys are in progress.

(5) A stacked rotating bipolar electrode cell is being tested for the recovery of copper from dilute cupric sulfate solutions.

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

Oral Presentation

On the Growth Mechanism and Structures of Sulfide Scales on Fe–Cr Alloys; T. Narita, T. Ishikawa and K. Nishida: The 20th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1985.

Electrolysis of Dilute Cupric Sulfate Solution in a Stacked Rotating Bipolar Electrode Cell; Y. Shinno, T. Sasaki and T. Ishikawa: The 11th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan., 1985.

The Effect of Wall Materials on Performability of Self-Heating Simulated Cell; S. Konda, T. Narita and T. Ishikawa: The Meeting of Research Projects, Grant-in-Aid for Scientific Research (Energy), Feb., 1985.

Effect of Permeation of Chloride Melts on Heat Transfer Characteristics of Alumina Particles-Packed Cell Wall; S. Suzuki, S. Konda and T. Ishikawa: The 52nd Annual Meeting of Electrochem. Soc. of Japan, Apr., 1985.

Development of Aluminum Electrowinning Process with Chloride Melts and Bipolar Electrode Cell (Part 7) Comparison of Heat Transfer Characteristics between Particles-Packed Cell wall and Tube-Stacked Cell Wall; K. Nishimura, S. konda, T. Narita and T. Ishikawa: *ibid.*, Apr., 1985.

Electrolysis of Cyanide Solution in a Stacked Rotating Bipolar Electrode Cell; T. Sasaki and T. Ishikawa; *ibid.*, Apr., 1985.

Effect of Phytic Acid on Copper Corrosion; T. Notoya and T. Ishikawa: The 50th Spring Meeting of Japan Chemical Society, Apr., 1985.

On the Fracture Strength of Ceramic-Metal Bondings; T. Narita, A. Kumatoritani, K. Kurokawa and R. Nagasaki: The 96th Spring Meeting of Japan Institute of Metals, Apr., 1985.

Phase Relationships of the Fe–Cr–S System at Low Sulfur Pressures; T. Narita, T. Ishikawa and K. Nishida: *ibid.*, Apr., 1985.

Ceramics-Metal Bondings by Prediffusion Method —Part II—; T. Takashima, T. Yamamoto, T. Narita and K. Nishida: *ibid.*, Apr., 1985.

Effect of Phytic Acid on Anodic Behavior of Copper in Borate Solution; T. Notoya and T. Ishikawa; 85 Spring Meeting of the Japan Society of Corrosion Engineering, May, 1985.

Inhibition Action of Some Organic Inhibitors in 70/30 Brass Dezincification ; T. Notoya and T. Ishikawa : 4th Asian-Pacific Corrosion Control Conference, May, 1985.

Electrodeposition of Titanium Borides from Fluoride Melts ; T. Narita, H. Sadamitsu, S. Konda and T. Ishikawa : The Spring Meeting of the Hokkaido Section of JIM, June, 1985.

The Effects of Surface Polishing on Fracture Strength of Ceramics-Metal Bondings ; T. Narita, A. kumatoritani and T. Ishikawa : *ibid.*, June, 1985.

Inositol and Inositol Phosphate Ester as Corrosion Inhibitors for Copper ; T. Notoya and T. Ishikawa : The Hokkaido Section Meeting of JIM, June, 1985.

Electrolysis of Dilute Solution of Cyanide in the Presence of Copper Ion ; T. Sasaki, N. Kanai and T. Ishikawa : 85 Hokkaido Section Summer Meeting of Japan Chem. Soc., July, 1985.

Effect of Phytic Acid and Benzotriazole on Anodic Dissolution of Copper ; T. Notoya and T. Ishikawa : The 32nd Symposium on Corrosion and Protection, Aug., 1985.

Sulfidation Behaviors of an Fe-2.25Cr-1Mo Steel in H_2S-H_2 Atmospheres ; T. Nartia and T. Ishikawa : *ibid.*, Aug., 1985.

On Testing Solution for the Study of Corrosion Behavior in Tap Water ; T. Ishikawa and R. Hatazawa : *ibid.*, Aug., 1985.

Development of Aluminum Electrowinning Process with Chloride Melts and Bipolar Electrode Cell(Part 8) Problems from Tube-stacked Cell Wall and the Resolution ; K. Nishimura, S. Konda, T. Narita and T. Ishikawa : The 1985 Fall Meeting of the Electrochem. Soc. Japan, Sept., 1985.

Electrochemical Treatment of Cupric Sulfate Solution with a Stacked Rotating Bipolar Electrode Cell(Part 6) Electrolysis in a Cascade System ; T. Sasaki and T. Ishikawa : *ibid.*, Sept., 1985.

Future Trends of Chemistry and Technology on Molten Salts ; T. Ishikawa : The 100th Meeting of the Committee on Molten Salt Chemistry, Oct., 1985.

Bondings of Si_3N_4 Ceramics and Stainless Steels with an Ti-Ni filler ; T. Narita, S. Konda and T. Ishikawa : The 97th Fall Meeting of JIM, Oct., 1985.

Ceramics-Metal Bondings with Prediffusion Method —Part III— ; T. Yamamoto, T. Takashima, T. Narita and K. Nishida : *ibid.*, Oct., 1985.

Creep Deformation and Sulfidation Behaviors of Fe-Cr Alloys in H_2S-H_2 Atmospheres ; T. Narita : The 110th Fall Meeting of ISIJ., Oct., 1985.

Development of Aluminum Electrowinning Process with Cloride Melts and Bipolar Electrode Cell (Part 9) On the Minimum Power consumption for Various Sizes of the Cell ; K. Nishimura, S. Konda, T. Narita and T. Ishikawa : The 18th Syposium on Molten Salt Chemistry, Nov., 1985.

Evaluation of Phytic Acid as a corrosion Inhibitor for Copper ; T. Notoya and T. Ishikawa : The 25th Meeting of Japan Copper and Brass Research Association, Nov., 1985.

On Corrosion Behaviors of Boiler Tubes —Sulfidation— ; T. Narita, T. Ishikawa and Y. Harada : The Fall Meeting of Hokkaido Section of JIM., Nov., 1985.

On the Bonding of Si_3N_4 and Metals ; T. Yamamoto, T. Takashima, T. Narita and K. Nishida : *ibid.*, Nov., 1985.

Sulfidation Properties of Chromium Carbides at High Temperatures ; T. Narita, K. Imai and K. Nishida : The 123 Meeting of High Temperature Materials, Nov., 1985.

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

S. Goto, J. Kitabuki, N. Kosai, T. Kosaki,
Y. Moriwaka and T. Maemichi

Our laboratory is mainly concerned with studies on corrosion of metallic materials used in nuclear industry, characterization and dissolution of iron rust components, performance improvement of hydrogen reservoir alloys, and development of computer-aided equipment for electrochemical measurements.

Research subjects in progress are summarized as follows :

(1) Corrosion study of SUS 304 stainless steel in organic and inorganic decontamination reagent solutions for primary water-coolant circuits of nuclear reactors was continued.

(2) Various kinds of iron oxides were synthesized by different preparation methods, and characterized by XRD, SEM, and BET surface area measurements. Dissolution was investigated in aqueous solutions of EDTA, citric acid, and oxalic acid.

(3) Non-electrolytic copper plating on nonstoichiometric FeTi hydrogen reservoir alloys was performed. Remarkable improvements were achieved in preventing the pulverization of these alloys during repeated cycles of hydrogen uptake and release.

(4) Computer-aided equipment was developed to observe electrochemical transients. For this purpose, a cyclic potentiostatic method was developed, utilizing a microcomputer, and the kinetic parameters of electrode processes were precisely determined from the electrochemical transient data. As an application, a rapid method was devised for measuring polarization characteristics.

Oral Presentation

Development of Hydrogen Storage Systems ; T. Mizuno : Seminar at Hydrogen Research Center (Texas, U. S. A.), Aug., 1984

Study of Iron Breakdown by Chloride in Borate Buffer Solutions by a Radiometric Method ; T. Mizuno and J. O'M. Bockris : Conference of Office of Naval Research (Texas, U. S. A.), Sep., 1984

Investigation of Cl^- Breakdown of Iron Passive Films ; T. Mizuno and J. O'M. Bockris : Conference on Corrosion of the Sea Water Systems (Washington, U. S. A.), Nov., 1984.

Adsorption and Absorption of Chloride Ions in Passive Iron Systems ; T. Mizuno, Jose L. Carbajal and J. O'M. Bockris : Seminar in Corrosion Research (Texas, U. S. A.), Dec., 1984.

Corrosion Behavior of SUS 304 Stainless Steel in Aqueous Solutions of Organic Acids ; K. Ogura, M. Moriya, T. Morozumi : The 20th Annual Meeting of the Corrosion Research Association In Hokkaido, Jan. 19, 1985

Néel Temperature Measurements of α-FeOOH : M. Taniguchi, H. Ohashi and T. Morozumi : The 1985 Winter Meeting of the Hokkaido Sections of the Japan Society for Analytical Chemistry and the Chemical Society of Japan, Feb. 8, 1985

Hydrogen Uptake Kinetics of Iron-Titanium Alloys ; K. Ito, H. Ohashi and T. Morozumi : As above, Feb. 8, 1985.

Identification of Amorphous Iron Rust Components by Superparamagnetism ; H. Ohashi, M. Otsuka, T. Itaya, M. Taniguchi and T. Morozumi : The 32nd Annual Symposium on Corrosion and Corrosion Protection, Aug. 25, 1985.

Corrosion Behavior of SUS 304 Stainless Steel in Oxalic Acid Solutions ; T. Morozumi, K. Ogura and M. Moriya, : As above, Aug. 25, 1985.

ELECTROCHEMISTRY LABORATORY

Prof. Dr. N. Sato, Assist. Prof. Dr. M. Seo
Dr. T. Ohtsuka, Mr. K. Azumi
and Miss J. Fujiwara

Visiting Research Fellow

Guo Jiaju

Students

N. Goto, X. Jiang, K. Takemasa, D. Murata
H. Ozawa and D. Inoue

The research activities of the laboratory continue to be directed towards a better understanding of the molecular processes involved in the corrosion and passivation of metals and semiconductors from the fundamental view points.

Passivity and Passivity Breakdown

Basic research has been devoted to studies of the process of passivation, the growth and structure of passive oxide films, the local breakdown of passivity, and the local corrosion process taking place at the passivity breakdown sites. Particular attention has been paid to the molecular fluctuation of the passive oxide film which would be enhanced by the adsorption of aggressive anions.

Passivation Film on Iron

The passivation film on iron has been studied by using electrode impedance and photo-electrochemical techniques as well as 3-parameter-spectroscopic reflectometry. It was found from electrode impedance measurements that the passivation film consisted of a highly defective n-type semiconductive oxide. The time decay of photo-induced current indicates the presence of a high concentration of the surface state on the film.

Application of Laser Raman Spectroscopy

The corrosion products formed from iron or copper under various conditions in aqueous and gaseous environments were distinguished from each other through their Raman spectra. Raman spectroscopy was applied to identify, under the in-situ condition, the composition of the surface oxide film anodically formed on titanium. The surface oxide film was found to be basically composed of an anatase type of TiO_2.

Tungsten Oxide Exhibiting Electrochromism

Electrochromic behaviour of the anodic oxide film formed on tungsten in sulphuric and perchloric acid solutions has been studied by ellipsometry, Raman spectroscopy and IR reflection spectroscopy. The oxide film was found to consist of highly hydrated W(VI) oxide containing a terminal W=O bond. The electrochromic reaction seems to occur through a proton attack on the terminal W=O as represented by

$$\mathrm{W(VI)=O} + \mathrm{H}^+ + e \longrightarrow \mathrm{W(V)-OH}$$

Surface Analysis of Metal and Alloys

The influence of the initial surface roughness on the composition profile broadening of an oxide film on chromium due to argon ion-sputter etching has been investigated by AES for chromium specimens subjected to different surface polishing before dry-oxidation. The depth-resolution of the Cr_2O_3/Cr interface improved with decreasing the initial surface roughness. Surface characterization of the ferritic stainless steels containing a minor amount of Nb and/or Cu, which were subjected to active dissolution or passivated in sulfuric acid solution, has been performed by AES to examine the synergetic effect of Nb and Cu on corrosion resistivity.

Surface Stress Measurement of Metal Electrodes

Peizo-electric measurements were carried out to observe the change in surface stress of gold electrodes in sulfate and phosphate solutions and of iron electrodes in pH 8.4 borate solution. The potential of zero charge (pzc) of gold electrodes, the pH dependence of pzc and the specific adsorption of solution anions were evaluated from the piezo-electric signals. Furthermore, the evaluation of the flat band potential of passivated iron electrodes was made from the piezo-electric signals during cathodic reduction of the passive films on iron.

Other Activities

In 1985, Dr. Ohtsuka attended the USA-Japan Seminar on Corrosion held in Nikko on March 10–13 and presented a paper entitled "Laser Raman Spectroscopy for In-Situ Study of Thin Corrosion Films on Iron". Dr. Seo visited the Royal Institute of Technology in Stockholm, Sweden, from March 17 to 30 for a Japan-Sweden collaborative research. Professor Sato attended the 4th Asian-Pacific Corrosion Control Conference held in Tokyo on May 26–31. Professor Sato also attended the 26th Corrosion Science Symposium held at University of Manchester Institute of Science and Technology in Manchester, England, on September 23–26, where he received the U. R. Evans Award and presented an award address entitled "Fundamental Concepts of Corrosion". He is the 10th receipient of the U. R. Evans Award. Professor Sato organized the 4th Japan-USSR Joint Corrosion Seminar on Characterization and Control of Metal Surfaces held in Tokyo on October 22–25.

The following scientists from over the sea paid the visit to this laboratory in the year of 1985: Dr. J. W. Harrell, Jr. from University of Alabama, U. S. A., on March 23; Professor H. Leidheiser Jr. from Lehigh University, U. S. A., on March 15–16; Dr. Z. A. Foroulis from Exon Research and Engineering Co., U. S. A. on June 2–3; Professor J. S. L. Leach from Nottingham University, England on November 11–14.

Oral Presentation

Spectroscopic Properties of Passivation Film on Iron; K. Azumi, T. Ohtsuka and N. Sato: The 11th Hokkaido Section Meeting of Electrochem. Japan, Jan. 18, 1985

Measurement of Surface Stress of Metal Electrodes; M. Seo, T.

Makino and N. Sato: The 11th Hokkaido Section Meeting of Electrochem. Soc. Japan, Jan. 18, 1985

Influence of Minor Alloying Elements on the Corrosion Resistivity and the Surface Composition of Fe-26Cr Alloy; M. Seo, Y. Sato and N. Sato: The 20th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan. 19, 1985

Assignment of Thin Corrosion Films on Iron; K. Kubo, T. Ohtsuka and N. Sato: The 1985 Winter Meeting of the Hokkaido Sections of the Japan Soc. for Analytical Chem. and Japan Chem. Soc., Feb. 7-8, 1985

Laser Raman Spectroscopy for In-Situ Study of Thin Corrosion Films on Iron; T. Ohtsuka and N. Sato: The USA-Japan Seminar on Corrosion, Nikko, March 10-13,1985

Effect of Mo Addition on the Selective Surface Oxidation of Fe-Cr Alloy; M. Seo, F. Baba and N. Sato: The 96th Spring Meeting of JIM, April 1-3, 1985

Detection of Change in Surface Stress of Metal Electrode by a Piezo-electric Element; M. Seo, T. Makino and N. Sato: The 96th Spring Meeting of JIM, April 1-3, 1985

Change in Complex Refractive Index and Thickness of Passive Film on Iron during Galvanostatic Oxidation; T. Ohtsuka, K. Azumi and N. Sato: The 52nd Meeting of Electrochem. Soc. Japan, April, 4-6, 1985

Behaviour of Iridium Oxide Electrode Observed by Electromodulation Infra Red Reflection Spectroscopy; R. O. Lezna, K. Kunimatsu, T. Ohtsuka and N. Sato: The 52nd Meeting of Electrochem. Soc. Japan, April 4-6, 1985.

A Study of Metal/Solution Interface by Surface Stress Measurements; M. Seo, T. Makino and N. Sato: '85 Spring Meeting of the Japan Society of Corrosion Engineering, May 15-17, 1985

In-Situ Identification of Thin Oxide Film on Iron—Effect of Water Vapor Pressure on the Composition; T. Ohtsuka, K. Kubo and N. Sato: '85 Spring Meeting of the Japan Society of Corrosion Engineering, May 15-17, 1985

Spectroscopic Properties of Iron Passivation Film; K. Azumi, T.

Ohtsuka, N. Sato : '85 Spring Meeting of the Japan Society of Corrosion Enginerring, May, 15-17, 1985

Optical Measurements of the Anodic Tungsten Oxide Film Exhibiting a Electrochromism ; N. Goto, T. Ohtsuka and N. Sato : The 1985 Summer Meeting of the Hokkaido Section of Japan Chem. Soc., July 27, 1985

Composition of Anodic Oxide Film on Titanium by In-Situ Raman Spectroscopy ; J. Guo, T. Ohtsuka and N. Sato : The 1985 Summer meeting of the Hokkaido Section of Japan Chem. Soc., July 27, 1985

Application of Spectroscopic 3-Parameter Reflectometry and Photo-Induced Current Method to the Study of Passivation Film on Iron ; K. Azumi, T. Ohtsuka and N. Sato : The 1985 Summer Meeting of the Hokkaido Section of Japan Chem. Soc., July 27, 1985

Corrosion Resistivity and Surface Composition of Ferritic Stainless Steels Containing Minor Alloying Elements ; M. Seo, Y. Sato, G. Hultquist, C. Leygraf and N. Sato : The 32nd Annual Symposium on Corrosion and Protection, Aug. 25-27, 1985

In-Situ Raman Spectroscopy for Composition Examination of Anodic Oxife Film on Titanium ; J. Guo, T. Ohtsuka and N. Sato : The 32nd Annual Syposium on Corrosion and Protection, Aug. 25-27, 1985

Galvanostatic Cathodic reduction Behabiour of Iron Passivation Film ; K. Azumi, T. Ohtsuka and N. Sato : The 32nd Annual Symposium on Corrosion and Protection, Aug. 25-27, 1985

U. R. Evans Award Address—Fundamental Concepts of Corrosion ; N. Sato : the 26th Corrosion Science Syposium, Manchester, England, Sept. 23-26, 1985

Optical and Electrochemical Studies on the Passivity of Iron ; N. Sato : Seminar in the Department of Metallurgy and Materials-University of Cambridge, Cambridge, England, Sept. 27, 1985

Piezo-electric Response to the Change in Surface Stress of Platinum Electrode ; M. Seo, T. Makino and N. Sato : The '85 Fall Meeting of the Electrochem. Soc. Japan, Sept. 30-Oct. 2, 1985

Semiconductive Properties of Passivation Film on Iron ; K. Azumi, T. Ohtsuka and N. Sato : '85 Fall Meeting of the Electrochem. Soc. Japan, Sept. 30-Oct. 2, 1985

A Spectroscopic Study of Anodic Oxide Films on Tungsten Exhibiting Electrochromizm ; N. Goto, T. Ohtsuka and N. Sato : The '85 Fall Meeting of the Electrochem. Soc. Japan, Sept. 30-Oct. 2, 1985

Piezo-electric Response to the Change in Surface Stress of Gold Electrode ; X. Jiang, M. Seo and N. Sato : The Fall Meeting of the Hokkaido Section of JIM, Nov. 14-15, 1985

Corrosion Science

Norio Sato

Chemical Education, **33**, 337 (1985)

The foundamental corrosion process of metals was reviewed. The corrosion process in aqueous solution includes two electrochemical reactions of $M \rightarrow M^{2+} + e$ (metal dissolution) and $1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$ (reduction of oxygen). The reactions in this local cell model are the same as those in the fuel cell using a oxygen-metal couple. There are two surface states of metals. In the active state the corrosion progresses at a relatively high rate, while in the passive state the corrosion almost stops owing to the formation of a protective oxide film of passivation on metal surfaces. The local corrosion processes like pit formation provide a large damage for the passive state of metal surfaces. (Japanese)

Effects of Oxygen Concentration on the Corrosion Behavior of Carbon Steel in High Temperature Water

K. Mabuchi, Y. Horii, H. Konno,
H. Takahashi and M. Nagayama

Critical Issues in Reducing the Corrosion of Steels,
Proceedings of USA-JAPAN Seminar,
Nikko Japan, March 1985

The corrosion rate and corrosion potential of carbon steel in high temperature water were measured as functions of 1) dissolved oxygen concentration, 2) temperature and 3) corrosion time. The structure and composition of the formed oxide were also examined by a) electron microscopy, b) X-ray differaction, and c) X-ray photoelectron spectroscopy. The factors controlling the corrosion rate are discussed. (English)

Measurement of Change in Surface Stress of Platinum Electrode

Masahiro Seo, Takamitsu Makino
and Norio Sato

Denki Kagaku, **53**, No. 4, 266 (1985)

The change in surface stress of platinum foil electrodes in sulfate solutions of different pH has been measured as a function of electrode potential by using a piezo-electric detector with a potential-modulation technique. Electrocapillary-like curves were successfully obtained from the measured piezo-electric signals. The potential of zero charge (pzc) of platinum electrodes and the pH dependence of pzc were evaluated from the piezo-electric response. (Japanese)

Inhibition of Dezincification Attack in 70/30 Brass by Organic Corrosion Inhibitors

T. Notoya and T. Ishikawa

Journal of the Japan Copper and Brass Research
Association Vol. 24, p. 46 (1985)

Inhibition action of five different types of copper and/or zinc complexing agents as dezincification inhibitors for 70/30 brass was investigated using a potentiostatic acceleration technique in aerated 0.5 M NaCl solution buffered by adding acetate buffer solution to obtain a constant pH 4.4 at 60°C. The potential of 70/30 brass electrode was maintained for 3 hours at a potential −200 mV vs. S. C. E., which was about 100 mV more anodic than its corrosion potential in the solution. Homogeneous dezincification layer of 20∼25 μm in thickness was formed in uninhibited solution under the test condition. Inhibitor performance was evaluated by solution analysis of dissolved copper and zinc, and also by amount of electric charge after addition of inhibitor during the anodic dissolution. Benzotriazole (BTA), mercaptobenzimidazole (MBI) and tolyltriazole (TTA) were found to be effective inhibitors not only for the initial stage of dezincification but also for the process of dezincification layer growth in 70/30 brass. Dimercaptothiadiazole (DMTDA) and mercaptobenzothiazole (MBT) were also effective inhibitors for the anodic dissolution but they are not as effective as BTA for the process of dezincification layer growth. The inhibition mechanism of these inhibitors is mainly due to protective layer formation of copper and/or zinc complex on the metal surface to stifle active paths for metal dissolution. Copper-inhibitor complex formed on the brass surface would be more protective than zinc-inhibitor complex. It is concluded that dezincification attack in 70/30 brass can be prevented by addition of most promising inhibitors such as BTA and TTA to dezincification-prone environments. (Japanese)

Inhibition Action of Some Organic Inhibitors in 70/30 Brass Dezincification

T. Notoya and T. Ishikawa

Proceedings of 4th Asian-Pacific Corrosion
Control Conference Vol. 2, p. 982 (1985)

Five different types of copper and/or zinc complexing agents as dezincification inhibitors for 70/30 brass were tested using a potentiostatic acceleration technique in areated 0.5 M NaCl solution buffered by acetic acid — sodium acetate buffer solution of pH 4.43. The potential of 70/30 brass electrode was maintained for 3 hours at a potential −200 mV vs. S. C. E. which was about 100 mV more anodic than its corrosion potential in the solution at 60°C. Dezincification layer of 20–25 μm in thickness was formed in the uninhibited solution under the test condition. Inhibitor performance was evaluated by solution analysis of dissolved copper and zinc and by amount of electric charge after addition of inhibitor during the anodic polarization. Mercaptobenzimidazole (MBI), benzotriazole (BTA) and tolyltriazole (TTA) were found to be effective inhibitors not only in reducing anodic dissolution of both copper and zinc but also in controlling dezincification layer thickness in 70/30 brass. Dimercaptothiadiazole (DMTDA) and mercaptobenzothiazole (MBT) are also effective inhibitors for the anodic dissolution but they are not as effective as MBI, BTA or TTA in the process of dezincification layer growth. The inhibition mechanism of these inhibitors is probably due to the formation of copper and/or zinc complex films on the metal surface. Copper-inhibitor complex formed on the brass surface appears to be more protective than zinc-inhibitor complex. The dezincification attack in 70/30 brass can be prevented by an addition of most promising inhibitors such as BTA and TTA to dezincification-prone environments. This is an alternative method to prevent dezincification attack in 70/30 brass. (English)

The Mechanism of Spontaneous Dissolution of the Air-formed Oxide Film on Iron in a Deaerated Neutral Phosphate Solution

Hidetaka Konno, Masato Kawai
and Masaichi Nagayama

Surface Technol., **24**, 259-271 (1985)

Pure iron was oxidized in air at room temperature for 3-14 days and was then immersed in a deaerated 0.1 mol l^{-1} phosphate solution at pH 7.0. The corrosion potential E_{corr} and the rate of dissolution of the oxide were measured as functions of the immersion time. It is proposed that the oxide film formed in air, which consists of an outer γ-FeOOH layer and an inner Fe_3O_4 layer, dissolves according to the following cell reactions : an outer cathodic reaction

$$\gamma\text{-FeOOH}+H_2PO_4^-+3H^++e\longrightarrow FeH_2PO_4^++2H_2O$$

with $E^\circ=1.049$ V, an inner cathodic reaction

$$Fe_3O_4+3H_2PO_4^-+8H^++2e\longrightarrow 3FeH_2PO_4^++4H_2O$$

with $E^\circ=1.177$ V, and the anodic reactions

$$Fe+2H_2O\longrightarrow Fe(OH)_2+2H^++2e$$

with $E^\circ=-0.104$ V and/or

$$3Fe+4H_2O\longrightarrow Fe_3O_4+8H^++8e$$

with $E^\circ=-0.085$ V in which the cathodic reaction determines E_{corr}. The cathodic reaction occurs at the oxide-solution interface by accepting electrons transported through the oxide, and the anodic reaction occurs at the metal-oxide interface to form oxide by reacting with OH^- and/or O^{2-} ions migrating through the oxide layer. Thus the proposed mechanism is rather different from the local action cell model. After the dissolution of the oxide film, the iron dissolves according to the following cell reactions :

$Fe + H_2PO_4^- \longrightarrow FeH_2PO_4^+ + 2e$

with $E^\circ = -0.505$ V and

$2H^+ + 2e \longrightarrow H_2$

with $E^\circ = 0$ V, where the anodic reaction determines $E_{corr.}$ (English)

Dissolution Behavior of Magnetite in EDTA Solutions with Different pH

Shin-ichi Takasaki, Hiroki Tamura
and Masaichi Nagayama

Boshoku Gijutsu, **34**, 222 (1985)

Magnetite particles were dissolved at 60～95°C for 9 h in EDTA solutions ($0 \sim 3 \times 10^{-2}$ mol•dm^{-3}) with different pH (0.1～11). In the absence of EDTA the dissolution proceeds only at pH below 2. When EDTA is present the dissolution proceeds up to pH 6, and in the pH region of 2～5, the dissolved Fe concentration is almost independent of pH. The dissolution involves a number of processes such as (1) transfer of Fe^{2+} and Fe^{3+} ions from magnetite to the solution, (2) chelation of the dissolved Fe^{2+} and Fe^{3+} ions with EDTA to form $Fe^{II}Y$ and $Fe^{III}Y$, and (3) air oxidation of Fe^{2+} and $Fe^{II}Y$ ions to produce Fe^{3+} and $Fe^{III}Y$. The concentration of dissolved Fe ions can be calculated as the sum of the equilibrium concentrations of the species, i. e., Fe^{2+}, Fe^{3+}, $Fe^{II}Y$, and $Fe^{III}Y$. The actual dissolution behavior was in good agrrement with the results calculated as a function of pH and the concentration of EDTA added. (Japanese)

Acid-base Dissociation of Surface Hydroxyl Groups on Manganese Dioxide in Sodium Nitrate Solutions

Hiroki Tamura, Masahiko Mitsuta
and Masaichi Nagayama

Bunseki Kagaku **34**, 627 (1985)

Manganese dioxide suspended in aqueous solutions is covered with surface hydroxyl groups formed by hydration. There are two types of surface groups; one acts as an acid ($\equiv MnOH_a$) and the other acts as a base ($\equiv MnOH_b$). Dissociation of these surface groups (release of H^+ and OH^- ions) produces negatively charged ($\equiv MnO^-$) and positively charged ($\equiv Mn^+$) sites. The difference in the amounts of positive and negative sites is the (net) surface charge, which is counter balanced by electrolyte ions with opposite sign in an electric double layer of the solution phase. This phenomenon is responsible for the ion exchange by manganese dioxide. In this investigation, the amount of surface charge per unit area, or the surface charge density, σ, was measured by acid-base titration. σ is zero at a certain pH (pzc), and becomes more positive or more negative as pH decreases or increases from pzc. It was also found that, with increasing concentration of sodium nitrate (ionic strength I), the absolute value of σ increases and pzc shifts slightly to lower pH. An equation was derived for the relationship between σ, pH and I by taking into consideration that 1) the coexisting electrolyte facilitates the acid-base dissociation of the surface by offering counter-cations or anions to the charged sites, and 2) the dissociation is electrostatically affected by σ. The equation well explains the values of σ measured in wide ranges of pH and I. (Japanese)

Laser Raman Spectroscopy of Aqueous Metal Ions Produced During Localized Corrosion of Stainless Steels

Jiaju Guo, Toshiaki Ohtsuka and Norio Sato

Boshoku Gijutsu (Corrosion Engineering), **34**, 449 (1985)

An attempt by using laser Raman spectroscopy was carried out to investigate the composition of solution concentrated in a crevice during crevice corrosion of Fe-19Cr alloy in 0.5 M NaCl aqueous solution. The Raman spectra of $FeCl_2$, $FeCl_3$, $CrCl_3$, $Fe(NO_3)_3$, and $Cr(NO_3)_3$ aqueous solutions at different concentrations were also measured in order to obtain the standard spectra for identifying the composition of the aqueous metal-chloride complexes in the crevice solution. In the solution of a model crevice cell the complex species of $[Fe(H_2O)_6]^{2+}$ and $[CrCl]_2(H_2O)_4]^+$ are detected in-situ after prolonged anodic dissolution of the alloy at $E=0.50$ V (vs. Ag/AgCl) for 220 h. (Japanese)

Critical Issues on Passivity

Norio Sato

Bull. Japan Institute of Metals, **24**, 724 (1985)

The historical background on the passivity on metals and semiconductors was critically reviewed. (1) Histrical backgrounds of metallic passivity. (2) Active and passive states of surfaces. (3) Surface oxide films. (4) Breakdown of the passive oxide films. (5) Surface passivation of metallic alloys and semiconductive alloys. (Japanese)

Passivity of Metals

Toshiaki Ohtsuka and Norio Sato

Bull. Japan Institute of Metals, **24**, 727 (1985)

The passivation of various metals is summarized. Recent advances of optical methods such as the spectroscopic ellipsometry and the modulation reflection spectroscopy in addition to the Mossbauer and SEXAFS techniques provide new features of the passive films from view points of the composition and the film thickness. Recent results obtained by the impedance and photo-current measurements on passivated electrodes show that the passive films are composed of highly defective semiconductive oxides. The discrepancy between the passivation behaviour of iron, cobalt, nickel, etc. is attributed mainly to the difference in electronic semiconductor conduction mechanism of the passive oxide films. (Japanese)

Impedance of Iron Electrode Passivated in Borate and Phosphate Solutions

Kazuhisa Azumi, Toshiaki Ohtsuka
and Norio Sato

J. Japan Inst. Metals, **49**, 729 (1985)

In order to characterize the semiconductive properties of the passivation film on iron, the impedance of iron electrode was investigated in borate and phosphate solutions at various pH values. The results were discussed as compared with thickness data previously obtained from 3-parameter reflectometry.

From the effect of frequency and potential on the impedance an equivalent circuit is postulated for a passivated iron electrode, which consists of a series connection of two parallel RC circuits. One component R_LC_L of the two parallel circuits which is predominantly responsible for frequencies lower than 100 Hz, characterizes the dielectric property of the passive film, whereas the other component R_HC_H which appears at higher frequencies corresponds to the oxide/solution interface.

From comparison C_L with the film thickness, the passive film is found to consist of an inner electron-conductive layer where no potential drop occurs and an outer carrier depleted layer where the electric field is of the order of $1 \times 10^8\,\mathrm{Vm^{-1}}$. The dielectric constant of the outer layer is also evaluated at about 40. The component R_HC_H is found to be sensitive to the anionic species present in the solution and is thus likely to be associated with an ionic adsorption-desorption process taking place across the electric double layer at the oxide/solution interface. (Japanese)

XPS Analysis of the Depth Direction Distribution of Boron in Passive Oxide Film on Iron Formed in a Neutral Borate Solution

Hidetaka Konno and Masaichi Nagayama

J. Metal Finish. Soc. Japan, **36**, 581 (1985)

Hydrogen-annealed 99.99% pure iron was anodized at 0.6 V vs. SCE for 60 min in a deaerated 0.15 mol/l borate solution (pH=8.43). The in-depth profile of boron in the formed oxide film was determined by XPS combined with stepwise removal of the oxide by cathodic reduction. A mathematical function was introduced to obtain the real depth profile from the measured values. The profile was in good agreement with the one obtained by SIMS, though the results by SIMS was not quantitative. It was found that B(III) was distributed in the outer part of the film at an average B/Fe atomic ratio of 0.17–0.18, whereas little or no boron was detected by XPS in the inner part. The total amount of B(III) in the film was estimated to be 0.25 mg/m^2 or ca. 1.7 mass%. These results demonstrate that, with a suitable film sectioning technique, it is possible to determine the distribution of ions in the depth direction by XPS even for oxide films with thicknesses as thin as the escape depth of photoelectrons. (Japanese)

An Auger Analysis of Anodic Oxide Films on Niobium

Masahiro Seo and Norio Sato

J. Metal Finishing Soc. Japan, **36**, No. 12, 592 (1985)

Depth profiles of anodic oxide films formed on niobium in 1 mol•dm^{-3} phosphoric acid and sulfuric acid solutions were measured by simultaneous use of Auger electron spectroscopy and argon-ion sputter-etching. The penetration-depth, τ_p, of phosphorus in anodic oxide films formed in phosphoric acid was nearly half of the whole film thickness, τ_t. The penetration of sulfur in films formed in sulfuric acid, however, was negligible. The relative Auger peak-to-peak height (pph) of Nb (167 eV)/Nb (197 eV) changed with the relative Auger pph of O (510 eV)/Nb (197 eV) suggesting the possibility of state-analysis from the relative change in niobium Auger pph. The anodic oxide films were identified by comparison with the depth profile of a standard Nb_2O_5 film as consisting of a hydrous outerlayer and an anhydrous inner layer of Nb_2O_5. The degree of preferential sputtering of oxygen component from the Nb_2O_5 film decreased with increasing kinetic energy of the argon-ion beam. (Japanese)

Depth-profiling of Surface Oxide Film/Metal Systems

Masahiro Seo and Norio Sato

Transactions JIM, **26**, No. 10, 747 (1985)

Depth-profiling of various surface oxide film/metal systems (Cr_2O_3/Cr, Fe_2O_3/Fe, NiO/Ni and Nb_2O_5/Nb) was performed with simultaneous use of Auger electron spectroscopy and argon-ion sputter-etching (1 kV, 4×10^{-5} A•cm^{-2}) to obtain fundamental knowledge necessary for quantitative analysis of steel surface layer in depth. The composition broadening at the film/metal interface was observed for all systems. The location of the film/metal interface, Z, and the depth-resolution, ΔZ, were determined by assuming that the composition broadening at the interface obeyed an error function.

The average sputtering rate, v, of surface oxide film was measured from a linear relation between the film thickness, L_f, ellipsometrically or coulometrically obtained and the location of the film/metal interface, Z, expressed in terms of sputtering time. The value of v decreased in the order of NiO (4.3 nm min^{-1}), Nb_2O_5 (4.0 nm min^{-1}), Fe_2O_3 (2.9 nm min^{-1}) and Cr_2O_3 (1.9 nm min^{-1}). The relative depth-resolution, $\Delta Z/Z$, plotted as a function of Z depended on the film/metal system and further, discussion was made on predominant factors influencing the depth-resolution. (English)

Ellipsometry

Toshiaki Ohtsuka and Norio Sato

Denki Kagaku (J. Electrochem. Soc. Japan),
53, 354 (1985)

Ellipsometric technique to characterize electrode surfaces was reviewed. (1) Princeple and theory. (2) Apparatus. (3) Growth of anodic oxide films on metals. (4) Multiple-angle-of-incidence method to determine the optical parameters more than three at the electrode surfaces. (5) Spectroscopic measurements to follow the semiconductive property of anodic oxide films. (Japanese)

Ellipsometric Study of Anodic Oxide Films on Titanium in Hydrochloric Acid, Sulfuric Acid, and Phosphate Solution

Toshiaki Ohtsuka, Minoru Masuda
and Norio Sato

J. Electrochem. Soc., **132**, 787 (1985)

The anodic oxide film on titanium has been studied by ellipsometry and SEM observation. *Ex situ* multiple-angle-of-incidence and *in situ* ellipsometric measurements allow the complex refractive index to be estimated at $n=2.3-2.9i$ for the titanium substrate and $\bar{n}=2.1-0.03i$ for the anodic oxide film at wavelength 546.1 nm. The anodic oxide film thickness increases linearly with potential in a range from -0.55 to 7.5 V (RHE) at the rate of 2.8 nm V^{-1} in phosphate solutions of pH 1.6–12.1, 2.5 nm V^{-1} in 0.1 M HCl solution, and 2.4 nm V^{-1} in 0.1 M H_2SO_4 solution. At potentials more positive than 7.5 V, the film breaks down, leading to the formation of a thick oxide film probably due to an increased ionic current through the breakdown sites. The film composition is estimated to be $TiO_2(H_2O)_{1.4}$ or $TiO_{0.6}(OH)_{2.8}$, which suggests the presence of hydroxyl bridge in its bonding structure. (English)

Investigation of Metallic Corrosion by Laser Raman Spectroscopy

Norio Sato and Toshiaki Ohtsuka

Japanese Scientific Monthy, **38**, 516 (1985)

The application of laser Raman spectroscopy to the investigation of metallic corrosion was summarized. The laser Raman spectroscopy possesses a large advantage to assign the composition of metallic corrosion products under the in-situ condition in corrosive gaseous and aqueous environments, because the excitation and detection for the Raman spectroscopy are made by use of visible light. The recent Raman spectroscopic works in the metallic corrosion field are introduced. (Japanese)

Laser Raman Spectroscopy for In Situ Study of Thin Corrosion Films on Iron

Toshiaki Ohtsuka and Norio Sato

Proc. of the USA.-Japan Seminar on Corrosion
Ed. by S. Haruyama and H. Leidheiser,
Jr. (1985) p. 275

The laser Raman spectroscopy has been applied for the detection and characterization of thin corrosion films formed on iron in air at a temperature range from 100 C to 150 C. It is found that the oxidation of iron in dry air leads to the formation of a surface oxide film which is magnetite and that the water vapor in air accelerates the formation of hematite. The ratio of magnetite to hematite in the surface oxide film appears to increase with increasing water vapor pressure, temperature, and oxidation time. (English)

Raman Spectroscopy of Anodic Oxide Films on HgTe

Masao Sakashita, Toshiaki Ohtsuka
and Norio Sato

J. Electrochem. Soc., **132**, 1864 (1985)

Laser Raman spectroscopic measurements of the anodic oxide film formed on HgTe in aqueous solutions reveal the characteristic Raman bands that appear at 422 and 684 cm^{-1}. These bands, which are different from those of crystalline $HgTeO_3$ and TeO_2 powders, may be attributed to a complex oxide of $HgTe_2O_3$ or an amorphous oxide of TeO_2 that might be formed in anodic oxidation. The heating effect on the anodic oxide film due to a focused laser beam is also discussed. (English)

pH Dependence of Thickness of Passive Film on Iron; Measurement by Three Parameter Reflectometry

Kazuhisa Azumi, Toshiaki Ohtsuka
and Norio Sato

Denki Kagaku (J, Electrochem. Soc. Jpn),
53, 700 (1985)

The thickness of passive films anodically formed on iron in phosphate (pH 3.1～6.5) and borate (pH 6.5～10.6) solutions was measured by using a three-parameter reflectometry. The thickness of films formed at constant potential for 3.6×10^3s increases linearly in the range from 1 to 5 nm with increasing anodic potential in the passive region. In acidic pH solutions lower than pH 5, the thickness of the film at constant overvoltage increases with increasing pH. In this pH region the thickness of the passive film remains unchanged with oxidation time after 3.6×10^3s potentiostatic oxidation, indicating that the film is in the stationary state where the rate of ion migration through the film (the ion migration current) is equal to the rate of ion transfer at the film/solution interface (the dissolution current). The pH dependence of the film thickness in this stationary state may be explained in terms of the fieldassisting ion migration through the film. In neutral and alkaline solutions, the pH-film thickness relationship at constant overvoltage exhibits a maximum thickness at pH 8.4. In this pH region the thickness of the passive film continuously grows even after 3.6×10^3s potentiostatic anodic oxidation. The pH dependence of this growing film thickness may be related to the amount of Fe ions dissolved and precipitated at the initial stage of oxidation, the amount of which depends on the solution pH. (Japanese)

Three-Parameter Reflectometry of a Passive Oxide Film on Iron in Neutral Solution

Kazuhisa Azumi, Toshiaki Ohtsuka
and Norio Sato

Denki Kagaku (J. Electrochem. Soc. Jpn),
53, 306 (1985)

A technique of three-parameter reflectometry has been developed to enable three unknown quantities of a surface film-refractive index (n_2), extinctive index (k_2), and thickness (d) to be evaluated without ambiguity by measuring three independent reflectivity changes ($\Delta R/R$), and has been applied to the study of a passive oxide film on iron in neutral solution. The n_2 of the passive film on iron was found to be 2.1 at potentials lower than 0.6 V and to increase with increasing potential up to 2.5 at potentials higher than 1.4 V. This indicates that the film formed at lower potentials possesses lower density because of the large amount of bound water in the film. Reflectometry during constant current-cathodic reduction showed that reduction takes place in two steps, suggesting that the film is composed of an outer layer with a relatively large value of n_2 and an inner layer with a small value of n_2. (Japanese)

Reaction of Porous Anodic Oxide Films on Aluminum with Hot Water V. Effects of Additives in Hot Water on the Hydration Behavior

Mitsuru Koda, Hideaki Takahashi
and Masaichi Nagayama

J. Metal Finish. Soc. Japan, **36**, 27 (1985)

Porous anodic oxide films formed on Al in an oxalic acid solution were hydrated in water at 99.5°C with and without additions of chromate, phosphate or nickel acetate. The hydrated films were then dissolved in a chromic acid-phosphoric acid solution. The changes in film structure during the hydration and dissolution experiments were followed by gravimetry and by impedance measurements in a neutral borate solution.

(1) As in pure hot water, pores of the film were filled up (or sealed) with hydrous oxide in a short time in waters containing chromate and nickel acetate, although slight dissolution of the film was observed. The water with phosphate did not hydrate the film but dissolved it to some extent.

(2) In the chromic acid-phosphoric acid solution, films hydrated in chromate-containing hot water dissolved faster and films hydrated in hot water containing nickel acetate dissolved slower than those hydrated in pure hot water. For all films, the dissolution rate was controlled by the dissolution of hydrous oxide which fills up the pores. The dissolution rate in general decreased with increasing electric resistance of the hydrous oxide.

The significance of the three existing methods of verifying the degree of "sealing", the coloring method, the impedance measuring method and the acid dissolution method, is discussed. (Japanese)

Estimation of the Microstructure of Anodic Porous Oxide Films on Aluminum by the Pore-filling Method

I. Analysis of Film Structure Formed by Two-Step Anodizing

Hideaki Takahashi, Hitoshi Kumagai
and Masaichi Nagayama

J. Metal Finish. Soc. Japan, **36**, 478 (1985)

Double layered porous oxide films were formed on aluminum by two step anodizing at an initial current density (i_1) in a H_2SO_4 solution (S-layer) and again at a second current density (i_2) in a $H_2C_2O_4$ solution (O-layer). The anodized specimens were re-anodized in a neutral borate solution at constant current density to follow the change in anode potential (E) with time (t). The geometrical structure of the double layered films was estimated by analysing the E–t curves (pore-filling method).

It was found that the structure of the O-layer was dependent on i_2 but independent of the structure of the S-layer formed at i_1. Pore-widening in the S-layer was observed to take place by chemical dissolution during the formation of the O-layer. (Japanese)

Surface Films Formed on Aluminum by Different Pretreatments

I. XPS Analysis of Thickness and Chemical Composition

Hideaki Takahashi and Masaichi Nagayama

J. Metal Finish. Soc. Japan, **36**, 96 (1985)

Pure aluminum was a) electropolished in $HClO_4/CH_3COOH$ solution (E. P.) or b) chemically polished in HNO_3/H_3PO_4 solution (C. P.) or c) immersed in H_3PO_4/CrO_3 solution after treatment E. P. or C. P.. The films formed were analyzed by XPS to estimate the thickness and chemical composition.

It was found that the thickness of the films was in the range of about 3.5 to 5.0 nm, and that appreciable amounts of electrolyte anions were included in the films. Except for phosphate the electrolyte anions included were found to be in reduced form.

The films formed by electropolishing consisted of aluminum oxide with small amounts of OH^- (or H_2O) and Cl^- ions, while those formed by chemical polishing included NO_2^- and PO_4^{3-} ions.

Immersion in H_3PO_4/CrO_3 caused the Cl^- and NO_2^- ions to disappear from the surface and films included high concentrations of OH^- (or H_2O). Cr^{III} and PO_4^{3-} ions. (Japanese)

Surface Films Formed on Aluminum by Different Pretreatments

II. Analysis of Film Structure by Measurement of AC Impedance and the Effect of Pretreatment on Subsequent Anodizing

Hideaki Takahashi, Tsuyoshi Hirose
and Masaichi Nagayama

J. Metal Finish. Soc. Japan, **36**, 149 (1985)

AC impedance analysis was carried out on the surface oxide films formed on aluminum by three surface treatments:

1) electropolishing, 2) chemical polishing, and 3) immersion in H_3PO_4/CrO_3 solution. The pretreated specimens were anodized in a neutral phosphate solution to examine the effects of the initial surface films on the subsequent formation of anodic oxide.

It was found that the equivalent circuits for the surface films were all expressed as parallel combinations of resistance (R_{ox}) and capacitance (C_{ox}) components. The value of R_{ox} decreased in the order of pretreatments (1)>(3)>(2); the order was reversed for C_{ox}. Dielectric constant and specific resistivity of the films were estimated and the relationship between the electrical properties and the chemical composition is discussed.

The Cl^- ions incorporated in the surface film formed by treatment 1) led to the formation of anodic oxide films with a relatively large number of defects. The inner layer of the anodic oxide films was composed of pure Al_2O_3, and it was thinner for films with pretreatment 3) than those with 1) and 2). This is explained in terms of the effects of pre-existing films on ion transport during subsequent anodizing. (Japanese)

The Effect of Water Vapor on the Oxidation of Type 430 Stainless Steel at 1,100°C

Hidetaka Konno, Tsuyota Shigekuni,
Hiroki Tamura and Masaichi Nagayama

Boshoku Gijutsu, **34**, 670-678 (1985)

Early stage oxidation behavior of type 430 stainless steel, at 1,100°C was examined by mass gain measurements, SEM observations, surface analyses with XPS, in-depth analyses with GDS, and EPMA line analyses. In dry air atmosphere, breakaway did not occur as expected, but when water vapor was introduced at $P_{H_2O}=0.20-0.03$ atm, it took place after an induction time, τ, of 30-90 min. It was found that, at a constant P_{O_2} of 0.16 atm, $1/\tau$ was proportional to $(P_{H_2O})^{0.5}$ but the rate of breakaway oxidation was independent of P_{H_2O}. The oxide film formed during the induction time had a single layer structure mainly consisting of Mn (II) and Cr (III) oxides, its morphology and elemental distribution in depth were very similar to those formed in the dry atmosphere. In the moist atmosphere, however, bound water was detected in the formed oxides. After the breakaway, the oxide film showed a two layer structure, an outer Fe oxide layer and an inner Fe–Cr oxide layer. These results suggested that water molecules function to deteriorate the protective Mn–Cr oxide which has been formed during the induction time and this leads to the breakaway. It is considered that water vapor is indispensable for the breakaway oxidation to proceed, but the rate is mainly determined by P_{O_2} if other conditions are fixed. (Japanese)

Sulfidation Properties of an Fe-23.4 Cr-18.6Al Alloy at Temperatures 1073 and 1173 K in H_2S-H_2 Atmospheres of Sulfur at Pressures 10^4-10^{-5}Pa

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

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An investigation is reported on the sulfidation properties of an Fe-23.4Cr-18.6Al(at.%) alloy at 1073 and 1173 K in H_2S-H_2 atmospheres, $10^4 > P_{S_2} \geq 10^{-5}$ Pa The sulfidation kinetics exhibited an early transient period before onset of parabolic kinetics. Values of the parabolic sulfidation rate constants increased by as much as 10^5 from their smallest values at low sulfur pressures, $P_{S_2} \leq 10^{-4}$ Pa, to maximum values at sulfur pressures $P_{S_2} \sim 10^2$ Pa. Multilayered scales were formed, the number and types of layers dependent on sulfur pressure. A fully developed scale at sulfur pressures $P_{S_2} > 10^{-3}$ Pa was composed of three layers; the inner and intermediate layers contained several quaternary sulfides, hexagonal $(AlCrFe)_2S_3$ and $(FeCr)Al_2S_4$, and spinels $(FeAl)Cr_2S_4$ and $(CrFe)Al_2S_4$, whereas the outer porous layer of isolated needles and plates was composed of FeS. This ternary alloy is shown to exhibit more superior sulfidation resistance than a binary Fe-26.6Cr alloy. (English)

High Temperature Sulfidation Properties of Fe-26.6 Cr and Fe-28.7 Mn Alloys in H_2S-H_2 Atmospheres

W. W. Smeltzer, T. Narita
and F. A. Elrefaie

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Sulfidation kinetics, morphological development and reaction mechanism for growth of sulfide scales on Fe-26.6 Cr and Fe-28.7 Mn alloys (alloying element in atomic %) were investigated at 973, 1073 and 1173 K in H_2S-H_2 atmospheres at sulfur pressures $10^4 > P(S_2) > 10^{-6}$ Pa.

In comparison to iron, the Fe-Cr alloy offers better sulfidation resistance only at pressures, $P(S_2) > 10^{-1}$ Pa and sulfidized at the same rate as pure chromium due to growth of protective chromium sulfide layers. Manganese offered more sulfidation resistance than chromium. The similar variation of sulfidation rates at low sulfur pressures indicates that growth of the single-phase scales is controlled by diffusion of alloying elements in the metal substrates. (English)

Sulfidation Properties of Chromium Carbides at High Temperatures

T. Narita and K. Imai and K. Nishida

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123 Meeting, Vol. 26, 595 (1985)

Sulfidation properties of chromium carbides $Cr_{23}C_6$ were investigated at a temperature of 1073 K in a H_2S–H_2 gas mixtures containing sulfur pressures from $10^{3.5}$ to 10^{-6} Pa. Sulfidation kinetics and scale structures were measured using T. G., X-ray Diffraction, EPMA and SEM–EDAX.

Sulfidation kinetics were catastrophic in nature at early reaction stages, whereas for long durations the parabolic and linear rate laws were observed at high and low sulfur pressures, respectively. Sulfidation products consisted of two scales : the outer scale composed of chromium sulfides with multi-layers and the inner scale of mixed phases of chromium sulfide and chromium carbide Cr_7C_3. This higher carbide was formed by reaction of $Cr_{23}C_6$ and C, which was released from sulfidation of $Cr_{23}C_6$ to form chromium sulfide and carbon.

Sulfidation rates of chromium carbide are low at high sulfur pressures, whereas it will become larger than those of Fe–Cr alloys at low sulfur pressures. It was suggested that grain boundary sulfidation is due to preferential sulfidation of chromium carbides precipitated along grain boundaries. (Japanese)

Study on the Energy Saving Process for Electrowinning of Liquid Aluminum from Chloride Melt

Tatsuo Ishikawa

YOUYUUEN (Fused Salt), 28, No. 3, 197 (1985)

In order to develop an energy saving process for electrowinning of liquid aluminum from chloride melt, firstly, a design rule for a bipolar electrode cell was discussed theoretically and suitable values of design parameters were determined experimentally.

Secondly, decomposition voltage of aluminum chloride and specific conductivity of the melt were determined at various concentration of aluminum chloride in the melt.

Finally, according to these values of the melt and the design parameters as well as an equivarent circuit of the bipolar electrode cell, bath voltages and cell efficiencies at various applied current were calculated without cell operation. The calculative procedures were confirmed by operating the laboratory-scale cells constructed with the proposed design rule. (Japanese)

Behavior of Nuclear Fuels During Reactor Accidents

Hiroshi Ohashi

Genshiryoku Kogyo, **31,** No. 2, 31 (1985)

When concerned with the behavior of nuclear fuels during reactor emergencies and accidents, it is of prime importance to know the mechanism and limits of damage to fuel cladding. It is also important to know effects on the primary system of the nuclear reactor and whether fuel claddings fail. In this review, phenomenological aspects of fuel behaviors are discussed according to a classification of reactor emergencies and accidents. Reactor emergencies and accidents are classified into (1) reactivity insertion events, (2) power cooling mismatches, (3) loss-of-coolant accidents, and (4) severe core damage accidents. Safety evaluation of reactor emergencies and accidents are classified into (1) abnormal power transients during reactor operation, (2) accidents, and (3) severe accidents and hypothetical accidents (site evaluation accidents). Items in both classifications are correlated and their significance in regulation procedures is discussed. The present status of the TMI-2 reactor is also presented. (Japanese)