FORWARD

Corrosion research in Hokkaido University was commenced in 1949 by a small group of workers. Incidentally, it was in the same year that CITCE was organized in Europe to provide an international meeting every year for the purpose of stimulating free discussions on various subjects of electrochemistry including corrosion of metals from the thermodynamic and kinetic standpoints of view.

The work carried out at the beginning was the measurement of polarization curves of iron in acid solution and the "rapid method", often called the transient method, was recommended as a reasonable method for measuring the anodic and cathodic polarization characteristics which determine the spontaneous corrosion state of iron. Thereafter, this method was applied to the study of the effect of organic inhibitors on the corrosion of iron and the anodic dissolution of nickel in acid solution.

In addition, the earliest potentiostat of electronic type in Japan was constructed by our group and proved the way for many advances in investigating the passivity of nickel and stainless steel before the subsequent spread of potentiostatic techniques in this country.

As our corrosion group grew up into several laboratories, the research activities rapidly increased with a variety of work including the electrochemical testing of painted steel and the mechanism of cavitation corrosion-erosion of steel. Practical corrosion problems which occurred in engineering and chemical industries in the district of Hokkaido have also been worked out by our group to give satisfactory settlements. During the period in the progress of corrosion research, the annual meeting of corrosion and corrosion control in Japan has been organized once a year, and the 20th meeting is coming soon in May this year.

Our corrosion research has continued more than twenty years with accumulation of research contribution. As an early organizer of our group, I express a great pleasure in the occasion that the first volume of the annual report of the corrosion research group in Hokkaido University is published on the background of twenty year research activity.

Tokyo,
January 1973.

Go OKAMOTO

Emeritus Professor of Hokkaido University,
The former President of the Corrosion
Research Association in Hokkaido.

FORWARD

Research work initiated twenty years ago by Professor Okamoto and continued by his corrosion group in Hokkaido University has attracted international attention of corrosion scientists and engineers. In the early stage the work was mainly restricted to the electrochemical study of corrosion of metals in aqueous solutions. With increasing the number of workers, however, the research activity has expanded into a variety of corrosion problems including dry oxidation of metals and alloys, and the corrosion research group in Hokkaido University is now one of the leading centeres of corrosion research in Japan.

It is hoped that the publication of the annual report of the corrosion research group contributes to the international cooperation of research activities on the corrosion science and engineering.

Sapporo,
January 1973.

Chikao YOSHII

Professor of Hokkaido University,
The President of the Corrosion
Research Association in Hokkaido.

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Current Activities

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. M. Nagayama, Assist. Prof. Dr. K. Goto,
Dr. T. Shiozawa, Mr. H. Tamura,
Mr. Y. Otake, and Miss K. Adachi

Students

H. Takahashi, H. Konno, N. Tanaka, A. Koike,
T. Maekawa, K. Hujioka, Y. Shizukuda,
and M. Mori

Research being made in this laboratory is mainly connected to the hydrolytic dissociation of metallic ions in aqueous solutions and to the mechanism of formation of oxide films at the metal/solution interphase. Investigations are carried out also on the inoganic corrosion inhibitors, the mechanism of plating reactions and the methods of analyses of metallic ions in various environments. Topics of present research concerning the corrosion of metals are as follows:

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

(2) Deposition of copper from Cu-pyrophosphate solutions. The cathodic polarization characteristics of Cu and the nature and the structure of the deposited layer are being examined as functions of the composition and the pH of the solution. Contribution of concentration polarization and the mechanism of reaction are investigated by using a rotating Cu electrode. Method of analysis of the solution composition has been developed.

(3) Estimation of corrosion velocity by the measurement of polarization resistance. Method of the measurement of polarization resistance of iron in neutral solutions is being investigated. The method of obtaining the relationship between polarization resistance and corrosion rate is also developed. Application of this method to the evaluation of corrosion inhibitors is found to be successful.

(4) Effectiveness of inorganic corrosion inhibitors. Minimum concentrations of chromate and phosphate required to inhibit the corrosion of steel almost completely are being measured as functions of concentrations of Cl^-, SO_4^{2-} and Ca^{2+} at a fixed pH of 8. The aim of this investigation is to predict the required amounts of inhibitors from the analyses of industrial water. At present, this is found to be successful for chromate when the concentration of this ion is relatively low.

(5) Air-oxidation of ferrous ion in neutral solutions. Rate of oxidation of ferrous ion is being measured as functions of the concentrations of ferrous ion, oxygen and pH of the solution. Effect of the nature and the concentrations of anions are also taken into consideration. The amount of the addition of OH^- ions required to keep the pH of the solution constant is measured by means of a pH-stat. The method of colorimetric determination of ferrous ions in the presence of a large amount of ferric ions has been developed.

(6) Chromium plating reactions from chromic acid solutions. Cathodic polarization curves of Pt and Fe electrodes are obtained in concentrated chromic acid solutions with and without addition of sulfuric acid. Rates of formation of Cr^{3+} and H_2 and the rate of deposition of chromium are measured at various cathode potentials. The purpose of this investigation is to clarify the mechanism of the plating reaction including the role of sulfate ion in producing bright chromium layers.

NONFERROUS EXTRACTION METALLURGY LABORATORY

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

Students

S. Katagiri, S. Suzuki, S. Izumoto, M. Ohgami,
and K. Harashima

This laboratory is concerned with basic and applied research on pyro- and hydrometallurgical extraction of nonferrous metals. Research in progress is concentrated on the following projects:

(1) Pyrometallurgy; Reduction kinetics of metal sulphides by hydrogen. This study is aimed at finding the mechanism of direct reduction of sulphide ores. Measurements of the reduction rate by thermobalance and Pirani gauge, direct observation of nucleation and growth by scanning electronmicroscope, phenomenological comparison of sulfidation and reduction, effect of impurities on the rate of reduction, and investigation of the mechanism of reduction at volatilization process of metal sulphides are being performed.

(2) Hydrometallurgy; Electrochemical measurements in some pressure hydrometallurgy. The reaction kinetics of the oxygen pressure leaching of sulphide minerals and the hydrogen reduction of metal salts in aqueous solutions are being studied by means of polarization measurements of sulphide and metal electrodes in autoclaves under the conditions of temperature up to 175°C and pressure of 50 kg/cm^2.

ELECTROCHEMISTRY LABORATORY

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

Students

T. Noda, Y. Shimizu, T. Tanigawa, T. Otsuka,
R. Nishimura, Y. Otake, N. Arayoma,
and M. Muroya

This laboratory is investigating the mechanisms of the reactions of metal surfaces with both aqueous and gaseous environments, the structure and property of passivation films on metals, the ion-exchange property of inorganic membranes, and the development of new ellipsometric techniques for metallic corrosion and oxidation studies.

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

(1) The composition and structure of anodic passivation films on iron in aqueous solution. Electrochemical and ellipsometric techniques are used to measure the composition and layer-structure of the films formed in borate-buffer and phosphate-buffer solutions in the wide range of pH from acid to base.

(2) Anodic oxidation of cobalt in aqueous solution. The anodic formation and cathodic reduction of the passivation film on cobalt in borate-buffer solution are being measured by means of coulometry, chemical analysis and ellipsometry.

(3) Ellipsometric measurements of passivation films on Fe–Ni alloys in aqueous solution. Films are produced by anodic passivation of Fe–Ni alloys in borate-buffer solution, and the relation between the film thickness and the alloy composition is being investigated.

(4) Properties of hydrous nickel oxide. Oxides are produced by precipitation in aqueous solution with or without subsequent aging, and the effect of water in the oxide on both the structure

and the physicochemical reactivity of the hydrous oxide is being determined.

(5) Anion-exchange properties of hydrous nickel oxide membranes. Oxide membrances are produced by precipitation on cellurose sheets, and anion-exchange is being determined with vari ous anions including halogen ions.

(6) Non-stoichiometry of silver oxide. The relation between the non-stoichiometry and the semi-conducting property is being investigated by use of electrical and electrochemical techniques.

(7) High temperature oxidation of iron and steel in the presence of water vapour and other contaminating gas such as sulphur dioxide and halogen. Oxidation kinetics is being investigated in the temperature range from 300° to 700°C by means of gravimetry and the effect of water vapour on both the kinetics and the oxide structure is being determined.

(8) Ellipsometric spectrometry. Improvement of ellipsometric techniques is being made to establish a new optical system of ellipsometer for spectral measurement of passive films on metals.

(9) Chloride-pitting of stainless steel. Rotating stainless steel electrodes have been used to measure the pitting current density and the rate of pit growth, and two different pitting mechanisms operating in different potential ranges have been proposed.

(10) Breakdown of passivation films. The breakdown has been theoretically investigated from the thermodynamic point of view and a mechanical mechanism for film breakdown has been proposed.

In addition, theoretical investigation is being made on the electrochemical thermodynamics and kinetics in connection with corrosion and oxidation of metals and membrane phenomena.

NUCLEAR REACTOR MATERIALS LABORATORY

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

Students

T. Mizuno, M. Moriya, E. Noda, T. Suzuki, H. Gotoh,
M. Koizumi, M. Kosuge, N. Takeuchi, M. Date,
K. Nakazawa, H. Nagashima, H. Narita,
and M. Mizuno

The laboratory is investigating several physico-chemical and electrochemical problems in the field of nuclear fuel and reactor materials engineering, including the corrosion and oxidation of metallic and ceramic reactor materials. Our concerns of corrosion and oxidation are listed as follows:

(1) Passivity of zirconium and its alloys in aqueous solutions. Electrochemical transients and A. C. impedance are measured in ammonium nitrate and other electrolytes. The cause of very peculier behavior of the oxygen evolution on passivated zirconium was clarified.

(2) Dissolution kinetics of zirconium into aqueous floride solutions. The rate of dissolution and some electrochemical characteristics are measured both in very diluted and concentrated floride solutions. The mechanism of electrochemical oscillation observed in these systems is being clarified.

(3) Hydrogen uptake into zirconium and titanium. The rate of hydrogen uptake into these metals, which is accompanied with corrosion and electrochemical polarization, is being measured in heavy water solution. The amounts of hydrogen absorbed in specimens are estimated by the nuclear chemical method with a deuteron accelerator.

(4) Oxidation of uranium dioxide. The effect of thermal history during the oxidation from UO_2 to U_3O_7 on the rate of oxidation from U_3O_7 to U_3O_8 is being investigated by using the thermo-

gravitational balance of Gulbransen type.

(5) Measurement of Mössbauer spectra of iron oxides and hydroxides. Various kinds of iron oxides and hydroxides were synthesized and the Mössbauer spectra of these compounds are being measured.

(6) Measurement of chemical activities of metal oxides in aqueous solution. The rate of reaction between iodide solution and various metal oxides are being measured with the electrochemical redoxstat, which was developed by our laboratory.

HIGH TEMPERATURE METAL CHEMISTRY LABORATORY

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

Students

G. Sasaki, A. Notoh, T. Yamauchi, N. Ohya Y. Sakon,
T. Inukai, H. Hagiwara, F. Satoh,
and H. Murohashi

This laboratory is investigating into the behavior of dry corrosion, that is, oxidation and sulfurisation, and also the diffusion in metals and alloys by means of solid couple and metallic vapor techniques. Furthermore, the decomposition of metal carbides in a wet atmosphere at room temperature and the diffusion mechanism of minor elements in iron and steel in molten state are also being studied.

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

(1) Kinetics of sulfidation of pure Fe, Fe-lowMn, Fe-lowNi, Fe-lowCr alloys and of oxidation of Co-lowNi and Ni-lowCo alloys: All these kinetics are checked by comparing their behavior with the postulates from the Wagner's new theory.

(2) Mutual diffusion in Fe sulfide–Cr sulfide systems: In order to clarify the growth mechanism of many kinds of scale layer found in the sulfidation of Fe–Cr alloys, an FeS–Cr_2S_3 couple is diffusion-annealed at 600 to 900°C. The diffusion is analyzed with an EPMA. For such analysis, the calibration curve of these quasi-binary sulfides is obtained by use of each synthesized compound.

(3) Oxidation of refractory metals and their prevention: Ta metal is siliconized, chromized, and aluminized by use of each metallic vapor at 1000°C, and the treated metal sheets are oxidized in air flow at 1000°C to compare their weight gains with that

of pure Ta metal. At that temperature the chromized Ta is found more protective than that of siliconized Ta.

(4) An oxidation mechanism applicable to the system showing a little complicated behavior is proposed by modifying the new theory after Wagner.

ELECTROMETALLURGY LABORATORY

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

Students

T. Sato, T. Ohkubo, M. Asakawa, T. Matsuda, T. Mihara,
S. Isagoda, G. Ohura, Y. Karikome,
Y. Kobayashi, and K. Sato

Research subjects in this laboratory are as followed:

(1) Structure and property of molten salt mixtures of aluminum chloride and alkali chloride are being estimated from the data of vapor pressure, equilibrium potential, transference number, and electrolytic conductance of these melts. The mechanism of anodic dissolution and cathodic deposition of aluminum in these molten salt mixtures is being clarified using rotating cylindrical electrodes by means of chronoamperometry, chemical analysis, and surface observation in situ.

(2) Electrodeposition of iron and hydrogen in acidic ferrous sulphate solution containing a metallic or metalloid ion, which functions to poison the hydrogen evolution, is being studied by means of coulometry and chemical analysis.

(3) Anodic dissolution and passivation of metals, mainly iron base alloys, are being investigated in molten alkali nitrates and nitrites by using potentiostatic, galvanostatic, and potential sweep methods. The corrosion products formed on the surface of the metals and dissolved in the melts are analyzed by X-ray diffraction, X-ray microanalysis, and chemical analysis. Corrosion tests in the melt are also carried out to compare with the data given by electrochemical techniques.

(4) Corrosion rate of iron and steel and of copper alloys under various heat transfer conditions is being determined at various temperatures by colourmetric analysis. Electrochemical

measurements are also being carried out under these conditions.

(5) Electrochemical studies on the passivation process of stainless steel and of pure chromium in acid solution are being performed by measuring the response of anodic current to temperature change at various passive potentials.

PHYSICAL METALLURGY LABORATORY

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

Students

K. Takahashi, Y. Kori, T. Nakai, K. Konno,
M. Kato, S. Ishiyama, M. Kobayashi,
and N. Hashimoto

Main research activities of this branch are concerned with the structural defects of pure iron, ferrous alloys, and other metals, and their influence on mechanical behavior. Electron microscopes of ordinary type and high voltage type are used to examine the structural defects. Especially, defects produced by irradiation of accelerated electron or neutron are intensively investigated.

Corrosion research activity is concentrated to the stress corrosion cracking of austenitic stainless steels. A high speed elongation technique is successfuly applied to analyze the anodic dissolution and repassivation processes on emergent slip steps of strained alloy. The other research subjects on corrosion are the followings:

(1) Stability of passive films on stainless steel in relation to its structure and composition. Stability of passive films formed on stainless steel in sulphuric acid solution is found to change with the formation condition, i.e., temperature, time, and potential. Changes in the structure and composition of each film are analyzed by means of ESCA, and other methods.

(2) Effect of minor elements on stress corrosion cracking of stainless steels. A high speed elongation technique is used to investigate the mechanism of stress corrosion cracking, the rate of which is controlled by minor elements, such as N and Mo, added to the alloy.

(3) Effect of nitrogen on pitting corrosion of stainless steel. Various levels of nitrogen content in the steel are obtained by

nitriding in a mixture of NH_3–H_2 gas and subsequent heat treatment. The pitting potential of the steels is being determined in 3% NaCl solution.

VACUUM SCIENCE LABORATORY

Prof. Dr. T. Yamashina, Assist. Prof. Dr. T. Hanasaka,
Dr. S. Tanaka, Mr. K. Watanabe, Mr. M. Nagasaka,
Mr. M. Hashida, and Miss Y. Sakai

Students

Y. Abe, T. Satake, and T. Honma

In this laboratory, research work on the reactivity of solid surfaces and vacuum engineering is in progress with the following subjects ;

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

(2) Effect of argon ion-bombardment on adsorption and catalysis of the evaporated nickel films. Clean films of nickel are ion-bombarded with argon. In order to clarify the nature of active sites, adsorption and catalysis by the films under very low pressures of hydrogen and deuterium are being measured by a mass spectrometer and a special pressure gauge.

(3) Reaction kinetics of titanium and zirconium with oxygen, nitrogen and hydrogen at very low pressures. Kinetic measurements of metals with various gases in the pressure range from 10^{-5} to 10^{-6} Torr and in the temperature range of 600° to 800°C are being made by means of a ultrahigh vacuum microbalance with high sensibility.

(4) Chemical reactivity of silver oxide films prepared by sputtering. Silver oxide films containing various amount of oxygen are prepared by the reactive-sputtering. The structure and property of the films have been studied by the infrared and X-ray diffraction techniques. Chemical reactivity of the oxygen in the sputtered films with ethylene is being examined.

(5) Development of residual gas analyzers as a small mass spectrometer. The reproducibility and stability of mass spectra of a quadrupole mass filter and an omegatron for various kind of gases have been examined under a specified operational condition for the purpose of obtaining fundamental data to the quantitative measurements as mass spectrometers.

(6) Precise measurements of adsorption of active gases and very small surface area of solids. A sensitive pirani gauge, by which the pressure of active gases such as H_2, O_2 and etc. can be measured precisely (10^{-1}–10^{-7} Torr) without any pumping action, has been developed. And a new apparatus for the rapid measurement of small surface area of solids was constructed, by which the size of surface area ($\sim 10\ \mathrm{cm}^2$) can be determined precisely in only half an hour, by using the pirani gauge.

(7) Mechanism of formation of oxide films by the reactive-sputtering. Molybdenum, titanium and silver oxide films containing various amount of oxygen have been prepared by means of the reactive-sputtering method. The structure and chemical composition of the films in the partial pressure of oxygen with the argon plasma is being investigated.

Oral Presentations

ANALYTICAL CHEMISTRY LABORATORY

Effect of Co-existing Substances on the Air Oxidation of Ferrous Ions; H. Tamura, K. Goto and M. Nagayama: The 1971 Winter Meeting of the Hokkaido Branches of the Japan Anal. Chem. Soc. and the Japan Chem. Soc., Feb. 1971.

Application of an Automatic Measurement of Freezing Point Depression to the Study of Hydrolytic Polymerization of Al Ions in Aqueous Solutions; T. Ishi, K. Goto and M. Nagayama: Ibid., Feb. 1971.

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Dissolution Behavior of Cathode Film Formed During Cathodic Reduction of CrO_3; M. Izumiya, H. Konno, M. Nagayama: Ibid., May 1971.

Change of the Nature of Porous Oxide Film on Al During Sealing Treatment: K. Yamada, K. Tamura, H. Takahashi and M. Nagayama; Ibid., May 1971.

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Effect of SO_4^{2-}, Cl^- and Ca^{2+} Ions on the Inhibitive Action of Chromate for the Corrosion of Steel: The 18th Annual Sympos. on Corrosion and Protection, Aug. 1971.

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Anodic Oxidation Behavior of Al in Phosphoric Acid Solution; H. Takahashi and M. Nagayama: The 39th Annual Meeting of the Japan Electrochem. Soc., Mar. 1972.

Cathodic Polarization Characteristics of Cu in Pyrophosphate Solutions; H. Konno and M. Nagayama: Ibid., Mar. 1972.

Effect of Phosphate on the Air-Oxidation of Ferrous Ions in Aqueous Solutions; H. Tamura, K. Goto and M. Nagayama: The 25th Annual Meeting of the Japan Chem. Soc., Apr. 1972.

Electronmicroscopy of Anodic Oxide Films on Al by an Ultra Thin Sectioning Technique. I. Structural Change of the Film

During the Current Recovery Period; M. Nagayama, H. Takahashi, H. Akaholi and A. Kitahara: The 28th Annual Meeting of the Japan Soc. for Electronmicroscopy., May 1972.

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Diffusion of Metals in Molten Sulfides; R. Shibayama, K. Jibiki, M. Sasaki and T. Tanaka: The 5th Symposium on Molten Salt Chemistry, Aug. 1971.

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ELECTROCHEMISTRY LABORATORY

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Passivation Films on Iron in Phosphate Solution; T. Noda, K. Kudo and N. Sato: The 18th Annual Symposium on Corrosion and Protection, Aug. 1971.

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ORAL PRESENTATION

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Corrosion Protection and Water Control in Hot Water Supply Systems; N. Sato: The Spring Course Sponsored by the Hokkaido Section of the Air-Conditioning and Sanitary Engineering Society, Apr. 1972.

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NUCLEAR REACTOR MATERIALS LABORATORY

The Possibility of Reaction of the Oxygen Reduction due to the Local Cathodic Reaction on Iron Rust; H. Ohashi, H. Goto, T. Morozumi : The 6th Annual Meeting of Corrosion Research Association in Hokkaido, Jan. 1971.

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Abstracts

Effect of the Potential of Etching Treatment and Passivation Treatment on the Stability of Passive Stainless Steels

T. Shibata and G. Okamoto

Corrosion Engineering (Boshoku Gijutsu),
21, 263 (1972), No. 6.

Stability of the passive 18–8 stainless steel in acid solution is found to depend on the potential during the etching treatment as well as the passivation treatment. The potential of the steel during the passivation treatment is controlled by changing the concentration of nitric acid solution or by using a potentiostat. Also a constant potential of the steel during the etching treatment is attained in a dilute nitric acid solution or in a concentrated sulphuric acid solution with or without applying the external polarization.

The stability which is represented by the self-activation time in oxygen-free sulphuric acid solution increases with increasing the potential of the passivation treatment, and a critical potential at which the stability abruptly changes is observed irrespective of the method of the passivation treatment, i. e., chemical passivation or potentiostatically controlled passivation. Structural changes of the passive film are concluded to take place at this critical potential of 0.4 volt (vs. SCE). The etching potential also changes the self-activation time of the passive steel treated at a constant passivation condition. The maximum stability is obtained at −0.32 volt of the etching potential. This fact is explained by assuming the selective enrichment of chromium on the surface before passivation. (Japanese)

Mechanism of the Dissolution of Porous Oxide Films Formed on Aluminum in Oxalic Acid Solutions

(1) Effect of Current Density and Temperature

M. Nagayama, K. Tamura, and H. Takahashi

J. Electrochem. Soc. Japan (DENKI KAGAKU),
39, 111 (1971), No. 2.

Effect of anodic current density and electrolyte temperature on the formation and dissolution behavior of porous anodic oxide films on aluminum was examined in dilute oxalic acid solutions. As is widely known, a considerable part of oxidized aluminum dissolves into the solution during anodizing with the formation of parallel pores in the oxide. It was reported previously that the total amount of dissolution is the sum of the amounts dissolved from the pore-walls and that dissolved from the bottoms of pores. In this investigation, the rate of dissolution from the pore walls V_s (cm/min) was determined by electron microscopic observation of films stripped from anodized specimens that had been immersed in the solution for various periods of time on open circuit. The rate of dissolution from the bottoms of pores V_b (cm/min) was then obtained by calculation using the value of V_s and the relation between the total amount of dissolution and the anodizing time. The number and radius of pores and thickness of oxide were measured and taken into consideration in the calculation. The values of V_s and V_b were shown to be constant all through the experiment for a given anodizing condition. In general, V_b is several times higher than the rate of film growth dh/dt (cm/min), which is also constant during anodizing. V_s does not change at all when the current is interrupted.

It was ascertained that V_s increases with rising electrolyte temperature. The apparent energy of activation was about 15 kcal/mole for c.d. of 9.4 mA/cm^2 and electrolyte concentration of 2%.

This means that the dissolution from the pore wall is undoubtedly a chemical process and its rate is controlled by a surface reaction. On the other hand, V_b increases remarkably with increasing c. d. and with lowering electrolyte temperature. These changes in the anodizing condition, as is well known, are accompanied by an increase in the potential difference across the barrier layer, so that it is reasonable to consider this type of dissolution from the pore-base to be an electrochemical nature. The mechanism explaining high rates of dissolution V_b from this part during anodizing is discussed in terms of a large transport number of aluminum ions through the barrier layer and the incorporation of protons from the electrolyte with vacancies of alnminum ions in the outermost part of the barrier layer. (Japanese)

Mechanism of Open-Circuit Dissolution of Porous Oxide Films on Aluminium in Acid Solutions

M. Nagayama, K. Tamura, and H. Takahashi

Corrosion Science, **12**, 133 (1972), No. 12.

When Al is anodized in acid solution, part of the oxidized Al dissolves into the solution with the formation of porous oxide film. Dissolution proceeds mainly at the bottoms of pores assisted by a high electrical field across the barrier layer. However, besides this type of 'electrochemical' dissolution, there is a 'chemical' dissolution occuring at the side walls of pores and the outermost surface of the oxide. It has been shown that the electrochemical dissolution of oxide at the pore-base stops instantaneously when the current is interrupted, whereas the behavior of the chemical dissolution scarcely changes. Accordingly, the amounts of electrochemical and chemical dissolution can be estimated separately by chemical analysis of the solution before and after stopping the anodizing current. Concerning the chemical or the open circuit dissolution, it was generally admitted that the time needed to dissolve the film nearly completely is almost independendent of the initial film thickness or the time of anodizing.

To explain this important experimental fact, two antagonistic concepts have been proposed. We have emphasized a 'simple pore-widening mechanism' in which the dissolution of pore-wall at a constant rate at any depth of pore is assumed. Diggle et al. have recently proposed the mechanism which will essentially be a 'pore-shortening mechanism'. They assumed a greater dissolution rate at the outer part of the film including the mouths of pores due to a greater diffusion rate of dissolved Al ions from this part. In this investigation, porous anodic oxide films were formed in sulphuric acid and oxalic acid solutions and the specimens were left immersed for different times on open-circuit after cutting the current.

Examination of electron-micrographs of the vertical sections of films showed that the open-circuit dissolution proceeds in such a manner that the pore widens at a constant rate at any depth of the pore and no appreciable change in the film thickness is observed. This is considered to be a conclusive evidence to support the mechanism we have proposed in preceding papers. (English)

Dissolution Behavior of the Barrier Layers of Porous Oxide Films during the Initial Period of Anodizing of Aluminum

M. Nagayama and H. Takahashi

J. Chemical. Soc. Japan, No. **5**, 850 (1972), May.

Anodizing of Al was carried out in oxalic acid-oxalate solutions over the pH range from 1.7 to 6.4 at constant anodic potentials and variations of the anodizing current, the structure of the film and the amount of dissolved Al ions were observed with time. The current-time curve was divided into four successive periods of a, b, c and d in relation to the surface structure of the film. In the initial period of anodizing (period a), the current falls nearly exponentially with time in accordance with the growth of the barrier layer. After a certain period of time the lowering of current ceases (period b) and the current begins to increase with time (period c) and finally reaches a steady value (period d), owing to the pore initiation and the growth of the porous layer. It was found that an appreciable amount of the film dissolves even in the period a ; the rate of dissolution is affected strongly by the anion species in the solution but scarcely changes with the pH of the solution. A high rate of dissolution observed at periods c and d increased remarkably with rise of anode potential and with fall of pH. This is explained in terms of the mechanism which assumes the formation of cation defects at the outermost part of the barrier layer and their interactions with protons in the solution. A new method of determining the barrier layer thickness of the porous type film was proposed. (Japanese)

CRGHU

Initiation of Chloride-Pitting Corrosion of Austenitic Stainless Steel in Sulphate Solution

N. Sato, K. Kudo, T. Sato, and G. Okamoto

Corrosion Engineering (Boshoku Gijutsu),
20, 15 (1971), No. 1.

Chloride-breakdown of the passivity of austenitic stainless steel in sulphate solution has been investigated by measuring the time, τ, required for initiation of pits after addition of chloride ion in solution as a function of electrode potential, solution pH and chloride ion concentration. The rate of pit-initiation, $1/\tau$, increases with the potential following a Tafel line with the slope, $\partial E/\partial \log (1/\tau)=0.3\,\mathrm{V}$, which is independent of pH in neutral and alkaline solution. As the concentration of chloride ion increases, the pit-initiation rate increases, holding the slope of Tafel line constant. The effect of chloride concentration on the rate at constant potential is represented by $1/\tau=k\,[\mathrm{Cl}^-]^2$, indicating that the process for breakdown of the passivity is a second order reaction with respect to chloride ion.

The solution pH does not affect the initiation of pits in neutral solution but appears to affect in acid solution ; the apparent effect in acid solution may be ascribed to the degree of association of SO_4^{2-} and H^+ which decreases with pH. The Tafel line of the pit initiation differs between the passive potential region and the transpassive potential region, though its slope remains constant. In the latter potential region the pit-initiation is hindered by CrO_4^{2-} ion produced in transpassive dissolution of the alloy. It is coexisting anions rather than hydrogen ion which determines the chloride-breakdown of the passivity of stainless steel.

The initiation of pits also appears to depend on the aging or thickness of the passivation film, its rate decreasing with extending the time of passivation. (Japanese)

Ellipsometry of the Passivation Film on Iron in Neutral Solution

N. Sato and K. Kudo

Electrochimica Acta, **16**, 447 (1971), No. 4.

Ellipsometric and electrochemical measurements have been made of the passivation film on iron during its potentiostatic anodic formation and galvanostatic cathodic reduction in borate buffer solution.

The complex refractive index estimated ellipsometrically of the cathodically reduced iron surface is identical with that of iron. indicating absence of any oxide films on it. The index of the passivation film comes close to that of spinel-type iron oxide, Fe_3O_4 or γ-Fe_2O_3. The passivation occurs at a minimum film thickness of about 9 Å and the film thickens up to 50 Å at the onset potential of oxygen evolution. The film thickness is in a linear relation with the oxidation potential in a limited potential region, which extrapolates to a film thicker than a monolayer even at zero anode overvoltage. The distribution of the potential in the film is discussed by a non-uniform film model consisting of an inner layer of intrinsic, anhydrous ferric oxide and an outer layer of hydrous, semiconducting ferric oxide.

Ellipsometric measurements also reveal that a surface film is formed on actively dissolving iron, and electrochemical measurements disclose transpassivation to occur above a critical potential in the oxygen-evolution region. (English)

A Fortran Program for Ellipsometry of Surface Films on Metals

K. Kudo and N. Sato

Bulletin of the Faculty of Engineering, Hokkaido
Uuniversity, No. **61**, 45 (1971), March.

The authors present a Fortran computer program for ellipsometry to analyse multiple absorbing films on metals by means of single reflection methods using an ellipsometer with a quater-wave plate on the side of the incident beam. This program makes it possible to calculate not only the theoretical reflection parameters as a function of the optical constant of the substrate and films, the film thickness of the uppermost and inner films and the angle of incidence, but also the optical constant and thickness of the surface films within a specified experimental error by comparing calculated reflection parameters with measured polarizer and analyser settings for a given surface. The program is applicable to any surface films particularly for the purpose of oxidation study of metals. (Japanese)

Note on "Temperature Dependence of Passive Film Growth on Iron at Constant Current" by R. V. Moshtev

N. Sato

Electrochimica Acta, **16**, 659 (1971), No. 5.

This article discusses an erroneous conclusion made by Moshtev on the mechanism of anodic growth of passive film on iron in neutral solution. Cohen and the author have previously proposed the place-exchange mechanism for the film growth, and there have been a dispute about the growth mechanism. In the above article Moshtev presented the experimental results and made a conclusion that the rate equation derived by Cohen and the author was in disagreement with his results. The author, however, points out that Moshtev's results can be reasonably explained by the place-exchange mechanism. (English)

Anodic Passivation Behaviour of Nickel in Neutral Solutions

N. Sato, K. Kudo, and M. Miki

Journal of the Japan Institute of Metals,
35, 1007 (1971), No. 10.

The anodic passivity of nickel in neutral solutions has been investigated by means of potentiostatic oxidation, galvanostatic reduction and chemical analysis techniques, and the thickness of anodic oxide film and the effect of solution pH and of anion species on the passivation behaviour are examined. The oxide film formed by anodic oxidation is difficult to be removed by cathodic reduction in neutral solution. To obtain a bare surface, the cathodic reduction has to be carried out in sulphuric acid for oxidized surfaces and either in acid or in neutral solution for electropolished surfaces.

In the passivity region, where NiO film is assumed to be formed, nickel dissolution is still observed during oxidation and the amount of nickel dissolved is dependent on the oxidation potential, the solution pH, and the anion species present. The film thickness estimated from coulometry in the pH range 5.5 to 9.5, however, is not practically affected by the solution pH and the anion species, but increases linearly with rise of the potential from 6 to 16 Å.

Above the potential of passivity region, the secondary passivation occurs where nickel dissolution is not detected. It is also shown that the secondary passivation is due to the formation of a higher valence nickel oxide, probably Ni_2O_3, which may be electrodeposited from dissolved Ni^{2+} ion in solution. The thickness, estimated from the potential decay curve of galvanostatic reduction, increases rapidly with rise of the potential and then decreases through a maximum. Further rise of potential results again in the dissolution of nickel, which is independent of the solution pH and the anion species.

ABSTRACTS

The growth kinetics of both the passivation film and the secondary passivation film is concluded to obey the inverse logarithmic rate law. (Japanese)

A Theory for Breakdown of Anodic Oxide Films on Metals

N. Sato

Electrochimica Acta, **16**, 1683 (1971), No. 10.

The author discusses the breakdown of anodic oxide films that results in pitting and transpassive dissolution, and presents a theory which describes thermodynamically the breakdown as a mechanical deformation or crack formation. The electrostriction pressure due to a high electric field of the order of 10^6 V/cm produces a compressive stress which could exceed the breakdown stress of oxide films. The surface tension stabilizes anodic oxide films, but this surface effect decreases with increasing film thickness. Thus, there is a critical thickness above which mechanical deformation or breakdown of the oxide film could occur. Anion adsorption lowers the surface tension and hence decreases the critical thickness for breakdown.

The net stress in anodic oxide films produced by electrostriction and surface tension is derived as a function of electric field, dielectric constant, surface tension, and film thickness. The breakdown potential at which the film thickness is critical is shown to depend on the anion concentration in solution. The theory is compared with experiments for the effect of halogen ion concentration on the breakdown potential and the effect of inhibitive anions on film breakdown of aluminum and stainless steel. Pore formation and transpassive dissolution of anodic oxide films are also discussed. (English)

The Anodic Oxide Film on Iron in Neutral Solution

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

Electrochimica Acta, **16**, 1909 (1971), No. 11.

The composition of the anodic passive oxide film on iron in neutral solution has been investigated by cathodic reduction, chemical analysis and ellipsometry. The cathodic reduction using a borate solution of pH 6.35 containing arsenic trioxide as inhibitor estimates iron in the film to be all iron (III), indicating that no magnetite layer is present in the film. Ellipsometry is used to estimate oxygen in the film, and it is shown that oxygen is in excess of the stoichiometric ferric oxide, suggesting the presence of bound water in the film. The average composition is represented as Fe_2O_3. 0.4 H_2O, in which hydrogen may be replaced partly with iron-ion vacancy. The anodic oxide film is composed of an inner anhydrous ferric oxide layer, which thickens with the potential, and an outer layer of hydrous ferric oxide whose thickness depends on the condition of passivation and environment.

The anodic oxide film formed in the oxygen potential region is also measured by cathodic reduction, and the film is found to maintain nearly constant thickness above a critical potential where transpassive dissolution begins to occur. (English)

Measurements of Anodic Oxide Films formed on Iron in Potential Regions of Passivity and Oxygen Evolution

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

Corrosion Engineering (Boshoku Gijutsu),
20, 525 (1971), No. 11/12.

Galvanostatic-cathodic reduction behaviour of anodic oxide films on iron has been investigated in neutral boric acid-borate solutions. The amount of iron cathodically dissolved from the film and the decay of potential during the cathodic reduction are much affected by both the solution pH and the cathodic current density. The current efficiency for the reductive dissolution of the film increases with lowering solution pH and attains 100% at $pH=6.35$. In the solution of $pH=6.35$, however, dissolution of iron substrate begins to occur immediately after completion of reduction of the film. Addition of arsenic trioxide into the solution is proved to inhibit the iron corrosion completely, and the maximum amount of dissolved iron from the film is now equal to the total amount of iron in the film calculated from the anodic film charge assuming the film as Fe_2O_3. This result not only provides evidence for the single hydrous ferric oxide layer model of anodic oxide films on iron, but also gives an electrochemical method for estimating the amount of iron in anodic oxide films on iron.

This method is applied to determination of iron in the films formed in the oxygen evolution potential region. It is shown that the film in the oxygen evolution region thicknes with rise of potential, but becomes thin at a critical potential where transpassive dissolution occurs. Further rise of potential results in a constant film thickness independent of the potential. (Japanese)

Ellipsometry of Anodic Oxide Films on Nickel in Neutral Solution

K. Kudo and N. Sato

Corrsion Engineering (Boshoku Gijutsu),
21, 24 (1972), No. 1.

Ellipsometric study combined with electrochemical measurements has been made on anodic oxide films on nickel in neutral sodium borate-boric acid solution in the potential regions of passivity and oxygen evolution. It is found that the oxide film once formed in anodic oxidation is not easily removed by cathodic reduction, and that the surface treated with potentiostatic reduction immediately after electropolishing gives good reproducibility in subsequent measurements. The reduced surface thus obtained is used as the optical reference. Films formed in the passive region are assumed to be NiO with optical constant of 2.7–0.25 i, and the film thickness is estimated which increases linearly with rise of the potential from 4 to 13 Å. The thickness is about 1.3 times thinner than that calculated from the anodic film charge assuming the film as NiO.

In the oxygen evolution potential region, the optical surface state is unsteady even after 1 hour anodic oxidation. It is shown, however, that the film in oxygen evolution changes in its optical constant and thickens rapidly with rise of the potential, and that at a certain potential the optical change begins to deviate from the expected direction of film growth. The film initially converts to a higher nickel oxide, probably Ni_2O_3, continues to grow up to a limiting thickness and finally takes a constant thickness independent of the potential. (Japanese)

Generation and Propagation of Chloride-Pits on Rotating Stainless Steel Electrode in Acid Solution

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

Transactions of the Japan Institute of
Metals, **1**, 103 (1972), No. 2.

This article describes the anodic pit generation and pit growth in 18–8 stainless steel at constant potential in sulphuric acid solution containing chloride ion, which were investigated by use of a rotating electrode. From systematic measurements of the time variation of pitting current and pit form, the authors make the following conclusions:

(1) The high speed rotation of electrode makes the pit growth very stable and enables the pitting dissolution current from a single pit to be measured. But little does it affect the pitting potential and the pit generation frequency.

(2) By use of rotating electrode it is made possible to measure readily the induction times for successively opening pits and hence the frequency of pit generation at constant potential.

(3) Potentiostatically, pits break out at a constant frequency and hence the number of pits n is a linear function of time τ_n,

$$n = k_p(\tau_n - \tau_0),$$

where the rate (or frequency) of pit generation k_p increases linearly with the potential.

(4) From the linear dependence of k_p on the potential, we may see that the process controlling the pit generation is electrical or electromechanical rather than electrochemical.

(5) An incubation time τ_0 is required for the onset of the linear get generation, which obviously differs from the inducition time τ_1 for opening an initial pit and which may be associated with establishing chloride ion adsorption equilibrium on or in the

passivation film.

(6) The pitting dissolution current from a single pit is in proportion to the area of pit mouth, and the current density is constant ($i_0 = 8$ A/cm^2) irrespective of the potential (+0.60 V∼+1.00 V (SCE)), indicating that the mass transfer of dissolving metal ion through the pit mouth is rate limiting. The metal ion concentration in the pit solution, estimated from $i_0 = 8$ A/cm^2, is so large (4∼20 mol/L) that a polymer of metal chloride or other metal salts can be deposited. We see therefore that the pitting dissolution in the potential range examined is similar to the electropolishing dissolution.

(7) The pit grows following a parabolic law in which the rate decreases inversely as the pit dimension, and the parabolic rate constant increases with the potential obeying a Tafel relation. From this we see that the field-assisting ionic migration through the pit is rate-limiting, and propose a pit model in which a thin barrier layer, continuosly forming and breaking down on the inner pit surface, assumes a high elecric field; a such layer may be called the transpassive film or electropolishing film.

(8) The from of pits is approximately hemispherical but the ratio of its depth to radius increases as the pit grows. (English)

Some Observations on the Interdiffusion between in the Fe and Fe–Al Alloy Systems

K. Nishida and T. Narita

Journal of the Japan Institute of Metals,
35, 269 (1971), No. 3.

Experiments were carried out so as to examine the basic multiphase diffusion behavior of Fe–Al alloys. At first, the etched structure and hardness of each intermetallic compound in the alloy were checked under the standard state. Then, the diffusion couples prepared by plating iron on alloys were heated at 800°C for 5 to 10 hr and at 610°C for 10 hr in case of the alloy containing an Al phase. lt was revealed that the ζ-phase ($FeAl_2$) showed an flat boundary with the α-phase and the η-phase (Fe_2Al_5) transformed in the sequence of η-ζ-α. In the latter case with minimum Al content, however, a considerable amount of the ζ-phase was formed between η and α phases and the ζ/η phase boundary showed an irregularity depending on the orientation of the original η phase. With more Al in the η phase, a new η phase protruded locally into an Fe layer and the ζ phase was formed much less. Especially, in the alloy with much higher Al contents such as those containing the θ phase as well as the η phase or both θ and Al phases, the local growth of the η phase results in the so-called bridge formation and in detachment of the plated Fe layer from the alloy substrate, with the formation of many voids in a newly formed η matrix. To explain the above phenomena, the change in volume accompanied on the phase transformation as well as the anisotropy of the η phase had to be taken into account. Some calculations by using of data about intermetallic compounds indicated that above behaviour is to be due to the high diffusivity of Al atoms released from the θ phase by the θ-η reaction or from an Al phase and also due to the creation of a new η phase at an Fe/alloy interface. (Japanese)

On the Corrosion of Fe–2% C–Al Alloys in Atmospheric Sulfur Pressure at 900°C

K. Nihida and T. Narita

Transactions of ISIJ, **12**, 422 (1972), No. 6.

2 wt % C-cast iron cotaining various Al amounts (0–25 wt % Al) were corroded under 1 atm of sulfur vapor by use of quartz ampoules at 900°C for various times up to 10 hr, and the decrease in thickness of substrate were measured in order to clarify the detailed mechanism of the corrosion of these alloys. Alloys with less Al content (1 to 4 wt % Al) having nodular graphitic substrate showed the greater corrosion obeying a linear rate law, and the strong anomalous scale growth of an inner layer was observed.

While, with more Al (more than 7 wt % Al) the corrosion kinetics was nearly parabolic, but after some time of corrosion it indicated the so-called "break away". The total scale thickness is very thin and also without any corner scale, but still the inner layer is very thicker than the outer one. From the above observations and the marker position found at the outer/inner layer interface, most of the scale were concluded to form with the inward migration of sulfur vapor through the scale which was very porous containing graphite particles and other sulfides besides pyrrhotite. (English)

On the Interdiffusion in α-Solid Solution of the Fe–Zn System by Means of a Vapor Method of Zn

H. Suzuki, Y. Masuda, and K. Nishida

Journal of the Japan Institute of Metals,
36, 509 (1972), No. 5.

The iron test piece was diffusion-annealed at 700 to 980°C in an evacuated two-stage capsule with pure Zn metal as the vapor source and each diffusion-penetration curve with the ordinate of a volume fraction unit was analized by means of Balluffi's method to determine the dependence of interdiffusion coefficients ($\tilde{D}$) on the concentration of Zn. The $\tilde{D}$ value at each temperature increased strongly with Zn concentration in the range of α-solid solution. The dependece of $\tilde{D}$ on temperature in the Arrhenius plot showed a good lineality, from which the activation energy for interdiffusion ($\tilde{Q}$) was calculated. The energy varied from 58 kcal/mol for 3 at % Zn to 46 kcal/mol for 18 at % Zn and was evaluated to be about 62.5 kcal/mol for the impurity diffusion of Zn in iron. Fine alumina markers placed initially on the test piece were found always on its surface after annealing, so that it is suggested that Zn atoms diffuse in predominantly in the α-range of an Fe–Zn system. The variation of frequency factor ($\tilde{D}_0$) with the activation energy for interdiffusion ($\tilde{Q}$) showed also a good linear relation, where the following equation would be held:

$$\ln \tilde{D}_0 = 3.2 \times 10^{-4} \tilde{Q} - 15.7\,.$$

(Japanese)

"Review on the Recent Research" On the Dry Corrosion

— Recent Approach and Prospective Expectation —

K. Nishida and T. Narita

Bulletin of Japan Institute of Metals,
11, 659 (1972), No. 9.

Since Tamman suggested a parabolic equation govering the thick scale growth at elevated temperature, more than 50 years have elapsed. During these five decades other many relations such as logarithmic and inverse logarithmic laws have been proposed. Such a trend of research on dry corrosions was reviewed mainly basing on theoretical treatment.

It was at first introduced that after Wagner proposed firstly the theoretical treatment on the above-stated parabolic rate law in 1933, many researchers made every endeavor to clarify the mechanism on the dry corrosions such as oxidation and sulfidation. However, in spite of such efforts the perfect expression valid for actual corrosion phenomena seems not to have been proposed yet, because the dry corrosion is so much complicated that it is much dependent on the relationship between the material and environment, nevertheless the gradual approach to the truth seemed to proceed by use of modern techniques, i. e., the developement of x-ray microanalysis, scanning electron microscopy based on the progress of the electron microscopy, and other analytical methods as well as in the electronic computation.

Further, it was introduced that Wagner proposed the analytical solution in 1952 to solve the kinetics of dry corrosion, but it contained many idealizing conditions which were modified later by others such as Whittle et al in England and Wulf et al in Australia. However, still these equations retain many points to be solved in order to apply the theory to the actual observations.

Very recently, Wagner suggested further a new theory to explain the idealized behavior of the scale in which one component of the alloy was too small to be effective to the bulk of oxide or sulfide scale. This is very useful to obtain the self-diffusivity of an alloying element in the host oxide without any use of radioactive tracers. Thus, lastly it was introduced that there were some experiments and reports trying to check that in what kinds of alloy system such an idealized condition will be valid.

There seems to be still a very long way to arrive at the final to explain perfectly the phenomena which have been already observed in the dry corrosion. However, such progressive statues as mentioned above will be expected to proceed step by step by means of more precise observations of the corrosion phenomena as they are, from simplicity to complexty of the process, and also with the application of both the physical and chemical data from other fields of science besides corrosion. (Japanese)

Kinetic Study on Reaction of Titanium with Low Pressure of Oxygen at High Temperature

M. Nagasaka and T. Yamashina

Journal of Vacuum Society of Japan
14, 320 (1971), No. 9.

The reaction kinetics of titanium foil with oxygen at very low pressures from 8×10^{-6} to 6×10^{-5} Torr has been studied in the temperature range of 475° to 890°C, by means of an ultrahigh vacuum microbalance. The rate of reaction was separable in two types, i. e., the linear rate law in the initial and the parabolic rate law in the latter period. The linear rate law was obeyed for longer times as the reaction temperature increased, the rate being almost unchanged within the temperature range of 475° to 890°C. In the initial linear part, the reaction rate was proportional to the oxygen pressure at each temperature which showed the linear oxidation to be controlled by the rate of arrival. The sticking probability and pumping speed per unit area (cm^2) for oxygen were constant with the change of oxygen pressure, e. g., 0.023 for the sticking probability and 0.45 liters/sec for pumping speed at 700°C.

On the bases of kinetic data including isothermal reaction rates with rapid change of oxygen pressure and vacuum annealing, discussion was made on the process of transformation in the reaction rate law. (Japanese)

Oxidation of Ti-15 Mo-5 Zr Alloy at Low Pressure of Oxygen ($4\times10^{-5}-2\times10^{-4}$ Torr)

M. Nagasaka, Y. Shikano, and T. Yamashina

Journal of the Japan Institute of Metals
36, 865 (1972), No. 9.

The oxidation kinetics of Ti-15 Mo-5 Zr alloy at low oxygen pressure of 4×10^{-5} to 2×10^{-4} Torr has been studied in the temperature range of 500 to 900°C by means of a microbalance. The results are summarized as follows. (1) The oxidation proceeded obeying to linear rate law for about six hours under the experimental condition of 600 to 900°C and 4×10^{-5} to 2×10^{-4} Torr. The oxidation rate of the alloy was observed to be lower than that of pure titanium at 700°C for each pressure. (2) The linear rate constant was proportional to oxygen pressure at each temperature, and therefore, the ratio of linear rate constant to oxygen pressure was found to be constant at each temperature, i.e., 7.9×10^{-5} for 600°C, 7.0×10^{-5} for 700°C, 6.4×10^{-5} for 800°C and 6.3×10^{-5} (g/cm^2/sec/Torr) for 900°C, respectively. As is obvious from these values, abnormality has been recognized in the temperature dependency on oxidation rate, that is, the rate decreased as the oxidation temperature increased. (3) The dependency of oxygen pressure on the oxidation rate was discussed on the assumption that the adsorption process of oxygen onto the metal surface might be rate determining. (Japanese)

Sorption of Nitrogen at Low Pressures by titanium

M. Nagasaka and T. Yamashina

Journal of Vacuum Science and Technology
9, 543 (1972), No. 1.

The sorption kinetics of nitrogen at pressures of 1×10^{-5} to 1×10^{-3} Torr on titanium foil was studied in the range 600°–800°C, by using an ultrahigh vacuum microbalance. In the similar way to oxygen, the rate law of nitrogen sorption was separable into two types, i.e., the linear rate law in the initial period and the parabolic rate law in the latter period. The linear rate law was obeyed for shorter times as the nitrogen pressure and the reaction temperature increased. In the initial linear part, the sorption rate was proportional to the nitrogen pressure at each temperature, which showed the linear sorption to be controlled by the rate of arrival. The sticking probability and pumping speed per unit area (cm^2) for nitrogen were constant with change of nitrogen pressure, e.g., at 800°C, 0.0045 for sticking probability and 0.098 (liter sec^{-1}) for pumping speed. The transition in the sorption rate laws and critical pressure of nitrogen for the transition are discussed on the basis of a diffusion theory. (English)

Changes in Roughness Factor of Glass Surfaces with Heating in a Vacuum

K. Watanabe and T. Yamashina

Vacuum **22**, 183 (1972), No. 5.

The changes in the roughness factor of glass surfaces with heating in a vacuum at 450°C were measured by xenon adsorption at liquid nitrogen temperature and their surface state were observed by means of electron microscopy. The roughness factor of Hario H-32 (H-glass) and soda lime glass (S-glass) increased at the first stage of heating and then decreased to the original value on further heating. On the other hand, the roughness factor of quartz glass (Q-glass) was found to be unchanged by heating. However, a remarkable change of the roughness factor in Q-glass was observed when it was heated together with H- or S-glass. Comparing the changes of roughness factor with the results of electron microscopic observation, it can be concluded that the changes of roughness factor are attributed to the creation and the disappearance of the rugged surface with heating. The rugged surface could be formed by crystallization of only thin surface layers. (English)

Studies on Metallic Corrosion in Molten Alkali Nitrates

Part V Oxidation of Iron in Molten Alkali Nitrate

T. Notoya and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
39, 930 (1971), No. 12.

The oxidation kinetics of iron in molten alkali nitrate was studied gravimetrically in the temperature range from 350°C to 470°C. It was found that the oxidation proceeds according to a parabolic rate law. The parabolic rate constant k depends on the temperature and the activation energy was estimated to be 33.8 and 35.0 kcal/mol. in $NaNO_3$ melt and in KNO_3 melt, respectively. An X-ray examination reveals that the oxidation product, iron oxide, formed on iron was magnetite. These results are compared with the oxidation kinetics of iron in dry oxygen or air. It is shown that either the acid or base has little effect on the iron oxidation in nitrate melt in the concentration range of acid or base from 10^{-3} and 10^{-2} mole fraction. (English)

Studies on Metallic Corrosion in Molten Alkali Nitrates Part IV Application of Measurement of the Anodic Oxidation Wave of the Nitrite Ion in Molten Alkali Nitrates to the Corrosion Reaction of Metals

T. Notoya and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
40, 104 (1972), No. 2.

The oxidation reaction of nitrite ion in molten alkali nitrates was investigated with a platinum microelectrode by means of a potential sweep method. The limiting current increased approximately linearly with the concentration of nitrite ion over a wide range of concentration, and decreased with the addition of a strong acid, $K_2S_2O_7$, to the melt. The effect of the potential sweep rate on the peak current was also examined. The activation energy for the limiting current of nitrite ion oxidation was 3.2–3.4 kcal/mol. Corrosion reactions of metals in the nitrate melt are expressed by the following equations.

Anodic reaction ; $Me \rightarrow Me^{n+}_{(oxide)} + ne$
Cathodic reaction ; $NO^{-}_{3(melt)} + 2e \rightarrow NO^{-}_{2(melt)} + O^{2-}_{(oxide)}$

In the course of iron oxidation, both $NaNO_2$ and Fe_3O_4 were produced stoichiometrically, although only insignificant amounts of other corrosion products such as NO, NO_2, O_2 and N_2 gases were observed to evolve on the specimen, indicating that the corrosion rate correspondes directly to the increase of the limiting current. In the oxidation of copper, nitrite formation is not stoichiometric due to the thermal decomposition of the nitrate melt during the oxidation reaction. The potential sweep method is recommended for corrosion studies in molted salts. (Japanese)

Studies on Metallic Corrosion in Molten Alkali Nitrates
Part VI Effects of Alkali Halide on the Corrosion of Iron and Low Carbon Steels in Molten Alkali Nitrates

T. Notoya, T. Ishikawa, and R. Midorikawa

J. Electrochem. Soc. Japan (DENKI KAGAKU)
40, 62 (1972), No. 1.

The effect of alkali and alkaline earth halides on the oxidation kinetics of iron and low carbon steels were investigated gravimetrically in molten mixtures of KNO_3 and $NaNO_3$ containing halide at 400°C. The corrosion of iron in the melts begins with pitting corrosion, then pits spreads over the entire surface. The corrosion rate of iron increases with increasing halide concentration and depends on the kind of anion as well as cation of the halide: aggressiveness increases in the order, $KCl>KBr>KI$ for anions, and $CaCl_2>BaCl_2>LiCl>NaCl>KCl$ for cations. This order is apparently related to the size of the halide ion in the melts. Chemical analysis and EPMA measurement indicate the presence of the halide in the oxide film formed in the melts. The corrosion resistance of low carbon steels containing 0.04–0.14% C is higher than that of pure iron. It is suggested that the corrosion behavior of metals in this system is similar to that of high temperature corrosion in an atmosphere containing halogen gas. (Japanese)

Beitrag zur Kinetik der Reduktion von Nickelsulfid mit Wasserstoff

T. Tanaka und H. Abe

ErzMetall, Bd. **25**, 181 (1972), H. 4.

Bericht über Versuche zur Bestimmung des Reaktionsmechanismus und der kinetischen Vorgänge bei der Wasserstoff-Reduktion von Nickelsulfid. Die Geschwindigkeit der Reaktion

$$1/2\,Ni_3S_2 + H_2 \rightarrow 3/2\,Ni + H_2S$$

wurde im Bereich von 500 bis 625°C an Nickelsulfidproben untersucht, die durch Sulfidierung von Nickelfolien bei 500 und 600°C oder durch Aufmahlen und Pressen von geschmolzenem Nickelsulfid hergestellt wurden. Der zeitliche Fortgang der Wasserstoffreduktion von sulfidierten Nickelproben ergab einen S-förmigen Kurvenverlauf, aus dessen linearem Mittelteil sich eine scheinbare Aktivierungsenergie von 21.9 kcal/mol ermitteln ließ. Durch eine Vorreduktion der Proben bis zu einem Reduktionsgrad von 5% konnte der durch eine zunehmende Reaktionsgeschwindigkeit gekennzeichnete Anfangsbereich übersprungen werden, so daß von Beginn an ein linearer Reaktionsverlauf zu verzeichnen war. Für die Vorreduzierten Sulfidproben ergab sich eine scheinbare Aktivierungsenergie von 27.2 kcal/mol. An Hand der Untersuchungsergebnisse und theoretischer Berechnungen konnte gezeigt werden, daß nicht die Desorption oder der Abtransport des gebildeten H_2S, sondern die Phasengrenzreaktion den geschwindigkeitsbestimmenden Teilschritt der Umsetzungen bildet. Dieses Ergebnis wird durch den hohen Wert der Aktivierungsenergie von 27.2 kcal/mol und die Abhangigkeit der Reduktionsgeschwindigkeit vom H_2-Partialdruck bestätigt.

A Discussion of the Mechanism of Oxygenation of Ferrous Ion in Neutral Solution

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

J. Electrochem. Soc. Japan (DENKI KAGAKU)
39, 690 (1971), No. 9.

The oxidation of ferrous ion by dissolved oxygen in neutral solutions has been studied by a number of investigators since the beginning of this century. The reaction is found to be of first order with respect to both ferrous ion and dissolved oxygen concentrations and of second order with respect to hydroxyl ion concentration ; namely,

$$-\frac{d[\mathrm{Fe(II)}]}{dt}=k_0[\mathrm{Fe(II)}]\,[\mathrm{O_2}]\,[\mathrm{OH^-}]^2 \qquad (3)$$

A value of $5.7\times10^{13}\,\mathrm{M^{-3}\,sec^{-1}}$ was obtained as the rate constant k_0 for a solution containing 0.01 M $NaHCO_3$ and 0.1 M $NaClO_4$ at 21°C. To explain the above rate equation, we have assumed that the first step hydrolysed ferrous ion $FeOH^+$ and the first step hydrolysed oxygen molecule O_2HO^- function as the reacting species. For the formation of these species

$$\mathrm{Fe^{2+}+OH^-=FeOH^+} \qquad K_{\mathrm{FeOH^+}}=[\mathrm{FeOH^+}]/[\mathrm{Fe^{2+}}]\,[\mathrm{OH^-}]$$

$$\mathrm{O_2+OH^-=O_2HO^-} \qquad K_{\mathrm{O_2HO^-}}=[\mathrm{O_2HO^-}]/[\mathrm{O_2}]\,[\mathrm{OH^-}]$$

in which $K_{\mathrm{FeOH^+}}$ and $K_{\mathrm{O_2HO^-}}$ designate their stability constants. By assuming that these species react in the rate-determing step (A), we have modified Weiss' reaction sequence as follows :

$$\begin{aligned}
&(\mathrm{A})\quad \mathrm{FeOH^+ + O_2HO^-} \xrightarrow{\text{slow}} \mathrm{Fe(OH)_2^+ + O_2^-}, &&\mathrm{O_2^- + H^+ \rightleftharpoons HO_2}\\
&(\mathrm{B})\quad \mathrm{Fe^{2+} + HO_2} \longrightarrow \mathrm{Fe^{3+} + HO_2^-}, &&\mathrm{HO_2^- + H^+ \rightleftharpoons H_2O_2}\\
&(\mathrm{C})\quad \mathrm{Fe^{2+} + H_2O_2} \longrightarrow \mathrm{Fe^{3+} + OH^- + OH},\\
&(\mathrm{D})\quad \mathrm{Fe^{2+} + OH} \longrightarrow \mathrm{Fe^{3+} + OH^-}
\end{aligned}$$

Thus, the rate of oxygenation of ferrous ion is

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = 4k[\mathrm{FeOH^+}][\mathrm{O_2HO^-}]$$

$$= 4k\,\mathrm{K_{FeOH^+}} \cdot \mathrm{K_{O_2HO^-}} \cdot \frac{[\mathrm{Fe(II)}]}{1+\mathrm{K_{FeOH^+}}[\mathrm{OH^-}]} \cdot \frac{[\mathrm{O_2}]\ \mathrm{total}}{1+\mathrm{K_{O_2HO^-}}[\mathrm{OH^-}]} \cdot [\mathrm{OH^-}]^2 \tag{2}$$

where $[\mathrm{Fe(II)}] = [\mathrm{Fe^{2+}}] + [\mathrm{FeOH^+}]$ and

$[\mathrm{O_2}]_{\mathrm{total}} = [\mathrm{O_2}] + [\mathrm{O_2HO^-}]$

It is shown by using the estimated values of k_0, $\mathrm{K_{FeOH^+}}$ and $\mathrm{K_{OHO^-}}$ that the theoretical equation (2) leads essentially the same equation as (1). The value of $\mathrm{K_{O_2HO^-}}$ is calculated to be in the range between $10^{-2,5}$ and $10^{-0.3}$. The large value of the specific rate constant k which lies between 4.6×10^9 and 1.4×10^{11} is explained by considering that the reaction is controlled by a diffusion process. Finally, the high reactivities of $\mathrm{FeOH^+}$ and $\mathrm{O_2HO^-}$ are interpreted in terms of the bridge mechanism of elcetron transfer between the complex ions. (English)

Determination of Rate of Water Uptake into Protective Paint Films by the Electric Capacitance Method

T. Morozumi and C. Fujiyama

J. Japan Soc. of Colour Material (Shikizai Kyokaishi)
44, 161 (1971), No. 4.

The electric capacitance method, which was originally proposed by Brasher and Kingsbury to determine the amount of absorbed water in a paint film, involves a few problems in its basic assumption. As an example, the water distribution in the paint film was assumed to be always uniform even when the stage of water absorption was transient. Therefore, the authors investigated the accuracy of the B–K method by the simulation with the digital computer and also by the immersion test.

Firstly, the distribution of water through the paint film was calculated on the basis of the one dimentional diffusion theory, and then the overall amount of water uptake W_1 was estimated by the integration as a function of time duration. Furthermore, the overall electric capacitance of the painted specimen was estimated by integrating the local electric capacitance which varied in accordance with the amount of absorbed water. The amount of absorbed water W_2 was again estimated from this ovarall electric capacitance by the ordinal B–K method. The comparison of the values of W_1 with that of W_2 revealed the fact that the error of the B–K method must be in practical quite small except the initial period of water absorption.

In the immersion tests of the painted specimens in the sodium chloride solution, however, a rather great discrepancy was found between the directly obtained water uptake by the weight method and the estimated by the electric capacitance method. Several reasons were speculated for explaining the observed discrepancy. In the most case, the plots of the weight and the electric capaci-

tance against the time nearly followed the analytical equations derived in this investigation as a rough approximation.

A method of estimation of the diffusion constant of water in the paint film was devised by using these analytical equations. By this method, the values ranging from 10^{-9} to 10^{-11} cm^2/sec was obtained as diffusion constants through various protective paint films from the observed electric capacitance time relations.

(Japanese)

Effect of Electrochemical Polarization on Hydrogen Uptake by Titanium in DCl–D_2O Solution

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Corrosion Engineering (Boshoku Gijitsu)
21, 256 (1972), No. 6.

The rate of hydrogen absorption into a potentiostatically polarized titanium was measured by using the nuclear chemical method, which was proposed in the previous report (this journal, **19**, 392–396 (1969)). The method consisted of the polarization, or the corrosion, of test specimen in a DCl–D_2O solution and the irradiation with accelerated deuterons of 10 to 150 keV from a Cockcroft-Walton accelerator. The amount and the distribution of the absorbed deuterium were determined by counting the number of neutron emitted by the $^2D(d, n)\,^2He$ reaction. The relationship between the deuterium distribution and the neutron count-deuteron energy characteristics was derived on the basis of the data of the cross-section of above reaction and the deuteron range given by Arnold and other investigators. The results of analysis were consistent with the observations. The proposed method can elucidate the amount of saturation and the rate of hydrogen uptake in the surface region within the depth less than about 1 micron.

Remarkable absorption was observed at more basic potential than -0.65 V vs S.C.E. and the rate of absorption increased with higher cathodic polarization. The composition of hydrogen-absorbed layer corresponded with a compound TiD_2. On the contrary, practically no absorption was observed at noble potentials. Three kinds of rate law, namely linear, parabolic and Fick's diffusion laws, were examined with the observed time rate of the increase of neutron evolution at a definite deuteron energy such as 100 keV. Among these rate laws, the linear rate law was found to be the most faborable one. These facts suggested that some electrochemical process on the surface of specimen controls the

overall rate of the hydrogen uptake. Relatively high proportion such as 40 to 50%, in comparison with the electrochemical evolution of hydrogen, was observed in the potential region ranging from −1.1 to −1.3 V. (Japanese)

Effect of Some Parameters on Reaction between Manganese Dioxide and a Potentiostatically Controlled Iodide-Triiodide Redox Systems

H. Ohashi and K. Hirohara

J. Electrochem. Soc. Japan (DENKI KAGAKU)
40, 610 (1972), No. 8.

The oxidizing capacity of manganese dioxide was investigated as a function of pH, iodide concentration, redox potential and other parameters by applying the controlled-potential iodometry.

The potential of $I^- - I_3^-$ redox electrode was controlled potentiostatically to keep the ratio of I^- vs. I_3^- constant. After the equilibrium condition was established and the electrolytic current became zero, a definite amount of MnO_2 powder was inserted into the electrolytic cell. In solutions the following reactions occurred ;

$$MnO_2 + 4H^+ + 3I^- \longrightarrow Mn^{2+} + 2H_2O + I_3^- \qquad (1)$$

$$MnO_2 + H^+ + 3/2\,I^- \longrightarrow MnOOH + 1/2\,I_3^- \qquad (2)$$

or

$$MnO_2 + xH^+ + 3/2\,xI^- \longrightarrow MnO_{2-x}(OH)_x + 1/2\,xI_3^- \qquad (3)$$

The consumption of I^- ion was compensated by the electrode reaction

$$I_3^- + 2e \longrightarrow 3I^- \qquad (4)$$

on the Pt gauze electrode by the aid of potentiostat. The reactivity of oxide against electrolyte was estimated from transient and steady value of electrolytic current.

Of all parameters mentioned above, the pH of solution had the greatest influence both on the degree of reaction and the decay characteristics of reaction rate. At pHs lower than 5, main reaction seemed to be a reductive dissolution and the MnO_2 specimen changed almost completely into Mn^{2+} within 4 hours in the

presence of excess iodide. The speculation was confirmed by the observation that total electricity was exactly equivalent to the amount necessary to the reductive dissolution of MnO_2 into Mn^{2+} ion. However, at pHs from 5.5 to 10, the amount of reacted MnO_2 at 4 hours reached only 15% of complete reaction at pH 5.5 and 0.5% at pH 10. This amount decreased remarkably with the increase of pH. At pHs higher than 11, reduction of oxide was restricted to quite a minor amount less than 0.5%. From this fact, it was concluded that the reduction at these pHs was confined to a few atomic layers of MnO_2 surface.

Concentrations of iodide higher than 0.1 mol/l exerted virtually no influence, but the reaction rate decreased with decreasing concentration below 0.1mol/l. The addition of Mn^{2+} ion exceeding 10^{-5} mol/l retarded the reaction rate to some extent, but the redox potential of the solution had no influence. The reactivity also varied with the origin of the MnO_2 samples.

The testing method presented in this paper would be applied to compare the reactivity of manganese dioxide of dry cell as well as other metallic oxides such as corrosion products. (Japanese)

Reaction Kinetics between Manganese Dioxide and a Potentiostatically Controlled Iodide-Triiodide Redox System

H. Ohashi

J. Electrochem. Soc. Japan (DENKI KAGAKU)
40, 681 (1972), No. 9.

Rate laws of reaction between manganese dioxide and a $I^- - I_3^-$ redox system were investigated on the basis of the observation presented in the preceding paper (J. Electrochem. Soc. Japan **40**, 610 (1972)).

In the presence of excess iodide the rate laws of reaction between manganese dioxide and a $I^- - I_3^-$ redox system were differed characteristically in the pH regions.

At pHs lower than 5, the reductive dissolution of MnO_2 predominated and the reaction rate followed approximately a linear law, such as,

$$1-(1-x)^{1/3}=k_1 t \qquad (1)$$

where x, k_1 and t were the degree of reaction, apparent rate constant and reaction time, respectively. The rate constant, k_1, was proportional to the square root of proton concentration. The activation energy was 5.4 kcal/mol at pH 4. These facts suggested a mechanism whereby the adsorption of a proton produced two active sites on the surface of MnO_2 and the escaping transfer of Mn^{2+} from the oxide surface to the bulk of solution determined the overall rate of reaction.

At pHs from 5.5 to 10, the reaction obeyed the linear rate law for an initial short period, and then the parabolic rate law. The latter law can be expressed by the following equation,

$$1-(1-x)^{1/3}=k_2 t^{1/2} \qquad (2)$$

An apparent rate constant, k_2, can be given by $(2DC)^{1/2}/r_0$, where D, C and r_0 denote the diffusion constant of proton, concentration of proton and the particle size of MnO_2, respectively. The change of rate laws with time was interpreted by assuming that a slight reductive dissolution occurred at initial period and the growth of a layer of indissoluble reaction products proceeded on the surface of MnO_2. The layer of indissoluble products may act as a barrier against the diffusion of the proton. The rate constant, k_2, was proportional to square root of proton concentration and activation energy was 5.1 kcal/mol at pH 7. Dependence of the rate constant on the concentration of proton was reasonably explained by assuming that the rate determining step was the diffusion process of proton through the layer of MnOOH. The diffusion constant of proton through MnOOH was approximately estimated to be 2.78×10^{-17} cm^2/sec at 30°C.

At pHs higher than 11, the reduction was restricted to the surface region of MnO_2 and proceeded according to the 1st order rate law.

In most cases, the adsorption of iodide ion, which played a role as electron donor, was found to be of Langmuir type.

(Japanese)

The Catalytic Exchange of Hydrogen-Deuterium on Copper-Nickel Alloy Plates after Various Surface Treatments

Y. Takasu and T. Yamashina

Bulletin of the Chemical Society of Japan
45, 2997 (1972), No. 10.

The catalytic activities of nine copper-nickel alloys (5 cm^2 in area) in hydrogen-deuterium exchange were examined at 1.5 Torr partial pressures of hydrogen and deuterium, using an ultrahigh vacuum apparatus incorporated with an omegatron mass spectrometer for continuous gas analysis. Without any surface treatment, the activity was greatest on pure nickel, decreased gradually as the content of copper in the alloys increased and virtually vanished in the alloys containing copper more than 70%. The activity of each alloy sample was observed to be extremely enhanced by a slight surface treatment of oxidation-reduction ($P_{O_2}=2.3$ Torr at 500°C for 1 min, $P_{H_2}=16$ Torr at 300°C for 2 hr). The activity of the 85% copper alloy after the oxidation-reduction treatment was greatest, one hundred times that of pure nickel. Annealing for a short time in an ultrahigh vacuum subsequent to the oxidation-reduction treatment caused the catalytic activity to decrease abruptly at a critical temperature (425°C). On the bases of the electron microscopic observation and the measurement of the surface roughness changed by the pre-treatments, the nature of active sites on copper-nickel alloys was discussed. (English)

Preparation of Molybdenum Oxide Films by means of Reactive Sputtering

T. Abe, T. Hanasaka, and T. Yamashina

Journal of Vacuum Society of Japan
15, 15 (1972), No. 1.

Molybdenum oxide films containing various amount of oxygen have prepared by means of reactive sputtering method. Changing the partial pressure of oxygen from 5×10^{-6} to 5×10^{-4} Torr in argon gas (total pressure is maintained at 5×10^{-3} Torr), the deposition rate, electrical resistivity, structure and chemical composition of sputterd films have been observed. When the partial pressure of oxygen in argon-oxygen mixtures was increased, the deposition rate of films began to decrease drastically at the same critical pressure of oxygen. Electron prove X-ray microanalysis showed that the content of oxygen in sputtered films was increased with the oxygen partial pressure. In the X-ray diffraction analysis, it was found that molybdenum oxide MoO_2 appeared suddenly in the sputtered films at the oxygen pressure of 1×10^{-4} Torr.

On the bases of the experimental data, discussion was made on the mechanism of oxide formation during the reactive sputtering. (Japanese)

Introduction to the Effect of Anions on the Corrosion of Metals

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Corrosion Engineering (Boshoku Gijutsu),
21, 107 (1972), No. 3.

The author discusses the effect of anions on the corrosion processes of metals from both thermodynamic and kinetic standpoints of view. The corrosion processes are classified into (a) the anodic dissolution of metal, (b) the oxidation of aquo-metal ion, (c) the hydrolysis of aquo-metal ion, (d) the polymerization of aquo-metal ion, (e) the anodic oxidation of aquo-metal ion and deposited metal salt, (f) the anodic oxidation of metal, (g) the dissolution of corrosion deposite and surface film, (h) the reductive dissolution of surface film, and (i) the cathodic reduction of oxidant. These corrosion processes are all related to the acid-base reaction involving either Brönsted acid or Lewis acid. Metal ions belong to the Lewis acid and may be classified into hard and soft acids depending on their tendency to combine with coordinate anions. The author therefore suggests an approach to the understanding of the anion effect on the corrosion processes from the acid-base reaction principles (Japanese).

Correlation between Thermodynamic Quantities of Adsorbed Oxygen and Selectivity for Ethylene-Oxide Formation on Silver

M. Seo and N. Sato

J. Electrochemical Society, Japan (DENKI KAGAKU)
40, 557 (1972), No. 8.

Oxygen adsorption on three catalysts of pure silver having different activities has been investigated in the temperature range 200°C～270°C by using a high sensitivity micro-balance. The thermodynamic quantities, such as differential free energy of adsorption ΔG_{ads}, differential heat of adsorption ΔH_{ads} and entropy of adsorbed oxygen S_{ads} at 230°C in case of the oxygen coverage $\theta=0.7$, are estimated. Comparison is made of the selectivity for ethylene oxide at 250°C with the thermodynamic quantity estimated at 230°C at $\theta=0.7$, and it is found that the selectivity for ethylene oxide increases with decreasing ΔH_{ads}, and increasing S_{ads}. Theoretical calculation of the entropy of adsorbed oxygen is also made and the adsorbed molecular oxygen $O^{-}_{2\mathrm{ad}}$ is shown to have the larger entropy than does the adsorbed atomic oxygen O^{-}_{ad}. It is likely that the selectivity for ethylene oxide formation is attributed mainly to the adsorbed molecular oxygen $O^{-}_{2\mathrm{ad}}$. (English)

Adsorption of Ethylene on Oxygenated Silver

M. Seo and N. Sato

J. Electrochem. Soc., Japan (DENKI KAGAKU)
39, 623 (1971), No. 8.

Ethylene adsorption on oxygenated silver in the presence and absence of oxygen gas has been studied by a continuous flow transient-response technique of gas chromatograph.

Ethylene is shown to adsorb on the oxygenated silver not only reversibly but also irreversibly in a temperature range from 40 to 100°C, but no adsorption occurs when the silver surface is reduced. The apparent equilibrium constants of ethylene adsorption on the oxygenated silver in the presence and absence of oxygen gas are estimated as functions of temperature, and the differential heat of the reversible ethylene adsorption is calculated. The ethylene content of adsorbed layer for the oxygenated silver in an equi-molar ethylene-oxygen gas mixture at 200°C is estimated to be about 12 wt %. (English)

Chemically Stimulated Exo-electron Emission from Silver Catalyst during Partical Oxidation of Ethylne

N. Sato and M. Seo

Journal of Catalysis, **24**, 224 (1972), No. 2.

Exo-electron emission from a silver catalyst during partial oxidation of ethylene has been studied by measuring simultaneously the exo-electron emission rate and the rate of ethylene oxide formation. The silver catalyst emits exo-electron continuously in a temperature range 150–210°C and its emission rate is proportional to the rate of ethylene oxide formation. The temperature dependence of the exo-electron emission obeys the Richardson relation for thermo-electron emission from semiconductor, whereas the rate of ethylene oxide formation fits to the Arrhenius equation.

This continuous exo-electron emission is discussed using a schematic diagram of electronic levels of the silver surface. The exo-electron emission from the silver catalyst during partial oxidation of ethylene is regarded as a thermo-electron emission from a thin semiconducting oxide layer on silver, the work function of which is reduced by adsorption of ethylene in the form of ethylene oxide. No exo-electron emission and no ethylene oxide formation are shown to occur from metallic copper, nickel oxide and iron oxide, with which only complete oxidation of ethylene proceeds. (English)