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and Miss. J. Fujiwara

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X. C. Jiang, L. Grasjo, T. Sakamoto, K. Araki, I. Sawamura,
T. Fujita, S. Ishiguro, K. Kishikawa,
K. Fushimi and M. Tsuji

The research activity of the laboratory continues to be directed towards a better understanding of the properties of interfacial phases on the surfaces of metals and semiconductors in relation to the interfacial electrochemistry involving corrosion and passivation.

Piezoelectric Responses to Surface Stress Changes on Metal Electrodes Covered with Oxide Films

Piezoelectric techniques combined with the admittance method have been applied to the study on iron and copper electrodes covered with oxide films in borate buffer solutions with and without sulphate ions. During cathodic reduction of the oxide film, the addition of sulphate ions enhanced the piezoelectric signals more on iron than on copper. The piezoelectric signals and admittance changed similarly with iron, indicating that the cathodic reduction of oxide film on iron proceeds at the film/solution interface. No significant effect of sulphate ions on the piezoelectric signals was observed for copper showing that the solid state mechanism is operative in the cathodic reduction of oxide film on copper. The potential of zero charge for iron and copper surfaces without any oxide films was also determined from the piezoelectric signals.

Electrochemistry of Nickel Base-Alloys in High Temperature-High Pressure-Aqueous Solution

The anodic polarization curves of Ni, Inconel 600 and 690 alloys were potentiodynamically measured in 0.5 wt% NaOH aqueous solution at 250°C to evaluate the corrosion resistances of these alloys. The surface characterization of the alloys subjected to the above corrosion environment was performed by Auger electron spectroscopy combined with argon-ion sputter-etching technique. The oxide films formed on Inconel 690 consisted of a double layer structure with a Ni rich outer layer and a Cr rich inner layer. The high corrosion resistance of Inconel 690 was ascribed to the double layer structure of the surface film.

Metal Oxide Films Prepared with Alkoxide-CVD

TiO_2 film was formed on aluminum substrate by CVD from titanium tetraisopropoxide (TTIP) to improve the pitting corrosion resistance of aluminum in neutral aqueous solutions. The depth-composition profile of the TiO_2/Al system was measured by Auger electron spectroscopy combined with argon-ion sputter-etching. From the measured composition profile, it was found that an oxidized aluminum layer was present between TiO_2 film and Al substrate. The pitting potentials of Al with and without TiO_2 film were potentio-dynamically measured in pH 8.4 borate buffer solution containing 10^{-2} M NaCl. The average pitting potential of Al increased by about 1.5 V due to the surface coating with TiO_2 film. The improvement in pitting corrosion resistance of Al with TiO_2 film was similar to that with Cr_2O_3 film previously reported.

In-Situ Gravimetry of Thin Metal Film by QCM

A quartz crystal microbalance (QCM) technique can detect a minute weight changes of a thin metal film from changes in the resonant frequency of the quartz crystal. The QCM technique was applied to investigate the absorption processes of hydrogen and deuterium into thin palladium electrodes during electrolysis. Changes in weight and resonant frequency deviated significantly from Sauerbrey's equation due to the stress created by absorption. The stress factors influencing the QCM results were evaluated from the relation between weight and resonant frequency for the α- and β-phases of the Pd-H or Pd-D system.

Electroluminescence from Silicon Electrode

Electroluminescence (EL) was detected from Si(111) p-type single crystals during anodic oxidation in ethylene glycol solution with KNO_3 containing Cl^- ions, to investigate the relation between the EL peak intensity and breakdown of the oxide film due to Cl^- ions. The EL peak intensity at 670 nm increased with increasing the concentrations of Cl^- ions up to a critical concentration of 2×10^{-2} M. At the critical concentration, the EL peak intensity increased rapidly prior to the breakdown of oxide film and then decreased abruptly after the breakdown. The rapid increase of EL peak intensity prior to the breakdown is associated with the incorporation of Cl^- ions in the oxide film which creates a large number of luminescence sources.

Transient Photocurrent of Passive Film on Metals

Transient photocurrent response to ultra-violet light radiated from nitrogen pulse laser (377 nm, pulse width 1 ns) was measured for the passive film on iron, nickel and titanium electrodes. For the titanium rapid increase and decrease of photocurrent were clearly observed when the electrode surface was illuminated by pulse light. The transient behavior was simulated by using a simple semiconductor/electrolyte model for analysis of electrochemical process at the electrode/solution interface.

Other Activities

In 1989, Prof. N. Sato and Dr. M. Seo attended the Annual Meeting (CORROSION/89) of NACE which was held in New Orleans, Louisiana, U.S.A. on April 17–21, 1989. At the NACE meeting, Prof. N. Sato received the Willis Rodney Whitney Award in recognition of public contributions to the science of corrosion and gave the Whitney Award Lecture entitled "Towards More Fundamental Understanding of Corrosion Processes". Dr. M. Seo also presented the invited lecture entitled "Inhibition in the Context of Passivation" by Prof. N. Sato and himself.

Prof. N. Sato organized the Sixth International Symposium on Passivity (Passivation of Metals and Semiconductors) which was held in Sapporo, Japan on September 24–28, 1989. This International Symposium was the first joint meeting of the two fields of metals and semiconductors which provided an opportunity for metal and semiconductor scientists to discuss the matters of common interest and to deepen their mutual understanding of the passivated state of solid surfaces.

At the beginning of October, 1989, Dr. T. Ohtsuka moved to the Department of Applied Chemistry at Nagoya Institute of Technology to get new position. Prof. J. W. Schultze from University of Dusseldorf, FRG, who was financially supported by The Ministry of Education, Science and Culture of Japan, stayed this laboratory for one month on September, 1990.

Oral Presentation

Application of Quartz Crystal Microbalance to the Study of Electrode Processes ; L. Grasjo, M. Seo and N. Sato : The 15th Hokkaido Section Meeting of Electrochem. Soc. Jpn., Jan., 1989.

Study of Adsorption of Cl^- ions on Gold Electrode by Piezoelectric Response ; X. C. Jiang, M. Seo and N. Sato : *ibid.*, Jan., 1989.

Surface Characterization of MOCVD-Cr Oxide Film on Al and the Corrosion Resistivity ; T. Sakamoto, M. Seo, N. Sato and S. Furuya : The 24th Annual Meeting of the Corrosion Research Association in Hokkaido, Jan., 1989.

Measurement of Minute Corrosion of Thin Metal Film by a Quartz Crystal Microbalance ; M. Seo, I. Sawamura, L. Grasjo, Y. Haga and N. Sato : The 149th Tech. Meeting of Corr. Eng. Div., The Soc. of Mater. Sci. Jpn., March, 1989.

Toward a More Fundamental Understanding of Corrosion Processes ; N. Sato : Annual Meeting of NACE (Corrosion/89), New Orleans, Louisiana, U.S.A., April, 1989.

Inhibition in the Context of Passivation ; M. Seo and N. Sato : *ibid.*, April, 1989.

Corrosion Measurement of Thin Copper Film in Nitrogen Gas and Air Containing H_2S by QCM ; M. Seo, I. Sawamura and N. Sato : '89 Spring Meeting of the Jpn. Soc. Corros. Eng., May, 1989.

Surface Coating with MOCVD-Metal Oxide Film on Al and the Corrosion Resistance; T. Sakamoto, M. Seo, N. Sato and S. Furuya: *ibid.*, May, 1989.

Dependence of Refractive Index and Thickness of Iron Passive Films upon the Oxidation Condition; T. Ohtsuka, K. Azumi and N. Sato: The 6th Intern. Sympos. Passivity, Sapporo, Japan, Sept., 1989.

An Overview on the Passivity of Metals; N Sato: *ibid.*, Sept., 1989.

Study on Electroluminescence from Si during Anodic Oxidation; M. Seo, K. Aotsuka and N. Sato: *ibid.*, Sept., 1989.

Analysis of Transient Photocurrent Measured on Passivated Iron Electrodes; K. Azumi, T. Ohtsuka and N. Sato: *ibid.*, Sept., 1989.

In-Situ Gravimetry of Passivation of Copper by Means of Quartz Crystal Microbalance; L. Grasjo, M. Seo and N. Sato: *ibid.*, Sept., 1989.

Piezoelectric Response to Surface Stress Change of Iron and Copper Electrodes Covered with Oxide Films; X. C. Jiang, M. Seo and N. Sato: *ibid.*, Sept., 1989.

Application of Quartz Crystal Microbalance to Minute Corrosion System; M. Seo. I. Sawamura, L. Grasjo and N. Sato: The 36th Symposium on Corrosion and Protection of Jpn., Oct., 1989.

Corrosion Test and Measurement of Thin Film; M. Seo: The 80th Corrosion Symposium of the Jpn. Soc. Corros. Eng., Nov., 1989.

NUCLEAR REACTOR MATERIALS LABORATORY

Prof. Dr. T. Morozumi, Prof. Dr. H. Ohashi,
Assoc. Prof. Dr. S. Sato, Dr. T. Mizuno,
Mr.K. Hirohara and Mrs. N. Ochiai

Students

S. Miyashita, N. Mura, M. Takada, S. Kanehira,
Y. Sugita, M. Yoneyama and M. Yoshida

The laboratory is concerned with investigations on corrosion of metallic materials used in nuclear industry, characterizations of iron rust components, development and improvement of hydrogen reservoir alloys, elucidation of the mechanism of pitting corrosion, migration of noble metal fission products in UO_2, and radioactive waste management.

(1) Magnetite and nickel ferrite were synthesized by several methods and characterized by XRD, SEM, Mössbauer spectroscopy, and surface area measurement.

(2) The dissolution rates of magnetite were measured in aqueous solutions of two kinds of decontamination reagents, EDTA and EDTA+N_2H_4, to determine the mechanism of dissolution of magnetite with the decontamination reagents.

(3) Structural changes of the $FeTi_{1.1}$ hydrogen reservoir alloy by thermal treatment, and by absorption and desorption of hydrogen were investigated. Changes in lattice parameters and Mössbauer spectra were determined as a function of annealing, and absorption and desorption cycles of hydrogen.

(4) Pitting corrosion of iron was investigated in buffered solutions by in-site radioactive tracer measurements. Growth of pits was explained by chloride ion accumulation and time variations in the current in pits. A two step theory was proposed, and it explained the process.

(5) Migration behavior of noble metal fission products in uranium dioxide was investigated by characterizing uranium dioxide pellets containing Pd and Mo, by measurements of O/U ratio and density, ceramographic observations, and EPMA.

Dr. M. Moriya resigned from the laboratory on March 31, 1989, and Dr. S. Sato joined as an Associate Professor on August 1, 1989.

Associate Professor Sato attended the 1989 Joint International Waste Management Conference in Kyoto in October. Dr. Mizuno attended the International Society of Electrochemistry 40th ISE Meeting in Kyoto in September, and the Sixth International Symposium on Passivity in Sapporo in October.

Oral Presentations

Transport Behavior of Cesium in Concrete ; R. Tutumi, S. Yonezawa, S. Sato and H. Furuya : The 1989 Annual Meeting of the Atomic Energy Society of Japan, Apr., 1989.

A Suggestion to Crud Chemistry ; T. Morozumi : The 4th Summer Seminar of the Atomic Energy Society of Japan on Nuclear Fuels, July, 1989.

Neutron Evolution from Palladium Cathodes in LiOD-D_2O Solution during Cathodic Discharge ; T. Mizuno, T. Akimoto and N. Sato : Mini Symposium of the Electrochemical Society of Japan, Cold Fusion and Electrochemistry, July, 1989.

Are There Unknown Phenomena in the Electrode Reaction of Hydrogen Electrodes? ; T. Mizuno : Seminar of the Heat Transfer Session of Japan Society of Mechanical Engineers, July, 1989.

What is the Cold Fusion? ; T. Mizuno : Seminar in Government Industry Deveropment Laboratory, July, 1989,

Neutron Measurement for Cold Fusion ; T. Mizuno : Seminar in the Forth Frontier Techno-Talk Meeting, July, 1989.

Newton Process : A Catalyst Regenerator ; M. Tamayama, A. Nishijima and T. Morozumi : The 4th China-Japan-U.S.A. Catalysis Symposium, Aug., (1989).

The Role of Oxide Films in the High Temperature Environments ;

T. Morozumi: The 1989 Summer Seminar of the Hokkaido Branch of the Surface Technology Association, Aug., 1989.

Research and Development in Europe on Geologic Disposal of Radioactive Wastes; S. Sato: Radioactive Waste Disposal Meeting, Radioactive Waste Management Center, Aug., 1989.

Neutron Evolution from Palladium Cathode in D_2O-LiOD Solution; T. Mizuno, T. Akimoto and N. Sato: International Society of Electrochemistry 40th ISE Meeting, Sept., 1989.

In-situ Analysis of Chloride Ion Concentration within Pits during Pitting of Iron; T. Mizuno: Sixth International Symposium on Passivity (Passivation of Metals and Semiconductors), Sept., 1989.

An Opinion in Relation to Studies of Cold Nuclear Fusion; H. Ohashi: The 6th Fall Meeting of the Plasma and Nuclear Fusion Society, Oct., 1989.

Distribution and Precipitation of Pd in UO_2; M. Takada, H. Ohashi. T. Morozumi, T. Ogawa and K. Fukuda: The 1989 Fall Meeting of the Atomic Energy Society of Japan, Oct., 1989.

Formation of $NiFe_2O_4$ in High Temperature Water; H. Ohashi, S. Miyashita, S. Shibata and T. Morozumi: *ibid.*, Oct., 1989.

Radiation Effects on Volumetric Changes and Corrosion for Simulated Radioactive Waste Glass; S. Sato, Y. Inagaki, H. Furuya and S. Sato: The 1989 Joint International Waste Management Conference, Oct., 1989.

Neutron Detection and the Mechanism of Cold Fusion; T. Mizuno, T. Akimoto and N. Sato: Phys. Soc. Japan, The Sectional Meeting, Oct., 1989.

Effects of Cr and Ti on the Hydrogen Absoprtion Behavior of the V Alloy; K. Aota, K. Kurokawa, T. Mizuno, K. Atarashiya and Takahashi: The Joint Fall Meeting of Hokkaido Sections of the Japan Insitute of Metals and the Japan Iron and Steel Institute, Nov., 1989.

ANALYTICAL CHEMISTRY LABORATORY

Prof. Dr. R. Furuichi, Assoc. Prof. Dr. H. Tamura,
Dr. H. Takahashi, Dr. H. Konno
and Miss R. Mizuguchi

Students

S. Kitazaki, S. Tamura, M. Tokita, K. Watanabe,
A. Furusaki, C. Ikegami, T. Sawaguchi
and H. Otsuka

This year, we received many scientists and engineers at home and abroad who are interested in our new photoelectron spectrometer (VG ESCALAB Mk II-MICROLAB Mk III combined system). Prof. J. W. Schultze from University of Dusseldorf visited our laboratory in September. The 6th International Symposium on Passivity was held in Sapporo in September, and Drs. Tamura, Takahashi, and Konno served as members of the executive committee. Dr. Tamura attended the 4th Battery Material Symposium held at York, U. K., in October.

The reserch programs in our laboratory are:

(1) *Characterization of iron oxides and oxyhydroxides.*

Different FeOOH powders are prepared from aqueous solutions with different aging periods in the solution and calicinated at different tempetratures. Surface and bulk characterization of the formed oxide powders were carried out by XRD, TG-DTA, BET method, and a quantiative analysis of the surface functional groups.

(2) *Reaction between metal oxide powders.*

The effect of the surface properties of starting materials on the powder reaction was examined for the Fe_2O_3-O_3-ZnO system.

(3) *Ion exchange with organic and inorganic exchangers*

Exchange of Na^+ with resin carboxylic protons and exchange of Co^{2+} with the protons of acid hydroxyl groups of MnO_2 were studied. It was found that an Na^+ ion exchanges with a proton of the resin carboxyl group and that there are two types of carboxyl sites with different reactivities and that a Co^{2+} ion exchanges with 1 and 2 hydroxyl protons of MnO_2 to form (1 : 1) and (1 : 2) surface complexes. For both exchanges the adsorbed metal ions suppress further exchanges. Models were developed to explain the stoichiometries and equilibria of the exchanges. These will serve to predict the extent of separation and recovery of ions in analytical chemistry and water treatment technology. The parameters in the models can also be used for the quality control of MnO_2 as a dry cell material and an inorganic ion-exchanger.

(4) *Synthesis of chemical manganese (IV) dioxide (CMD)*

Manganese (IV) dioxide was prepared by chemical (not electrolytic) oxidation of $MnCO_3$ which was formed by mixing an $MnSO_4$ solution and an NH_4HCO_3 solution. To oxidize $MnCO_3$, calcination at 350°C was conducted. The formed MnO_2 was examined as follows: morphology by SEM, specific surface area by the BET method, and ion exchange properties by titration. It was found that the oxide particles are porous spherical aggregates of much smaller particles and that their surface chemical properties are very similar to those of CMD commercially produced for dry cell use.

(5) *Formation of hydroxide films on aluminum in anion containing solutions at boiling temperature.*

Formation of hydroxide films on aluminum was investigated in $10^{-4} \sim 10^{-2}$ M phosphate, silicate, and citrate solutions at boiling temperature on open circuit by gravimetry, chemical analysis, impedance measurements, and XPS.

It was found that silicate and phosphate ions inhibit the formation of hydroxides more effectively at higher concentrations, and that citrate ions predominantly dissolve hydroxide at higher rates at higher concentrations. Impedance measurements suggested the existence of a thin oxide layer at the interface between hydroxide and the metal substrate, and XPS showed that large amounts of anions are incorporated in the outermost part of hydroxide films. A mechanism was proposed for the formation of hydroxide films by taking into account the roles of anions.

(6) *Anodizing of aluminum covered with thermal oxide films*

The formation of oxide films on aluminum was investigated by anodizing in a neutral borate solution at 80°C after pretreatment of thermal oxidation at temperatures between 500–600°C. Thermal oxidation was found to retard the dissolution of oxide during anodizing. The anodic oxide films formed after heavy thermal oxidation consisted of one layer of crystalline oxides and showed the small inverse electric field of 0.77 nm/V.

(7) *Anodizing of Al–Si die-cast alloy (ADC12) in sulfuric acid solution*

ADC 12 is a commercial Al-diecast alloy, which includes ca. 10 wt.% Si as well as small amounts of Cu, Fe, Mn, and Mg. Formation of porous anodic oxide films on ADC 12 was investigated by comparing that on Al–Si casting alloys. The effect of heat treatment on the film formation was also examined.

The steady value of the anode potential, E_a, for ADC 12 was observed to be much higher than that of the casting alloys. The growth rate of anodic oxide film on ADC 12 was considerably lower than that on the casting alloys, suggesting a higher rate of gas evolution during anodizing of ADC 12. Heat treatment of ADC 12 caused the film growth rate to increase and E_a* to decrease.

(8) *Formation of perovskite structure lanthanum chromium oxide films by electrodeposition.*

A method to form perovskite structure lanthanum chromium oxide ($LaCrO_3$ and $La_{1-x}M_xCrO_3$, M=Ca or Sr) films on metals was developed. The method consists of (i) the formation of precursor films, $(LaOH)_{1-x}M_xCrO_4\ nH_2O$, on metals by cathodic deposition from chromate solutions containing La and Ca or Sr ions, and (ii) the pyrolysis of the precursor films. The lanthanum chromium oxides are electron conductive and resistant to oxidation at elevated temperatures. The compounds are regarded as promising materials for solid oxide fuel cells. Further, $LaCrO_3$ was found to be a good coating material to protect alloys from high temperature oxidation. The protection mechanism of the coating was investigated for SUS 304 and SUS 430 stainless steels by XRD, GDS, and SEM.

(9) *Synthesis of perovskite structure lanthanum chromium oxide powders.*

A method to synthesize $La_{1-x}M_xCrO_3$ powders was developed using La(III), Cr(VI), and Ca(II) or Sr(II) compounds as starting materials. The method enabled the perovskite structure oxides to be formed with lower energy consumption than conventional methods. The formation mechanism was investigated by TG-DTA, XRD, IR, EPR, and chemical analysis.

(10) *Composition of oxide films formed during an initial period of high temperature oxidation.*

Composition of oxide films formed after 60s oxidation in H_2O-O_2 atmospheres at 1273 K was examined by XPS and XRD. The aim of the project is to understand the role of H_2O in breakaway oxidation. In the present work, a series of relatively pure Fe-Cr alloys were used as-rolled, and the use of commercial stainless steels and different pretreatments are also planned.

Oral Presentation

Formation of Perovskite Type Lanthanum Chromium Oxide Films Utilizing Electrodeposition; H. Konno, M. Tokita, S. Kitazaki and R. Furuichi: The 15th Meeting of the Hokkaido Sec. of Electrochem. Soc. Jpn, Jan., 1989.

Anodizing of Al-Si Casting Alloys in Sulfuric Acid Solutions; H. Takahashi, K. Watanabe, S. Hashimoto and R. Furuichi: The 24th Ann. Meeting of the Hokkaido Corr. Res. Assoc., Jan, 1989.

Determination of the Acid-Base Dissociation Constants of Surface Hydroxyl Groups on TiO_2 in Aqueous Solutions; H. Tamura, T. Oda and R. Furuichi: The 1989 Winter Meeting of the

Hokkaido Secs. of Jpn. Soc. Anal. Chem. and Chem. Soc. Jpn, Feb, 1989.

Adsorption of Arsenous Acid on MnO_2 ; N. Katayama, H. Tamura and R. Furuichi : *ibid.*

Effect of Heat Treatment of ADC 12 and Al/Si Alloys on the Formation of Porous Anodic Oxide Films in a Sulfuric Acid Solution ; K. Watanabe, H. Takahashi and R. Furuichi : *ibid.*

The Structure of Composite Oxide Films on Aluminum ; H. Takahashi : The 30th Ann. Meeting of the Hokkaido Sec. of Soc. Electron Microsc. Jpn., Feb., 1989.

Formation of Lanthanum Chromium Oxide Films on Metals Utilizing Electrodeposition and the Effect of the Film on Corrosion Protection ; H. Konno : New Materials Subcommittee Meeting of Hokkaido Sec. of the Jpn. Inst. Iron and Steel, Mar., 1989.

Anodizing of ADC 12 in Sulfuric Acid Solutions ; H. Takahashi, K. Watanabe, S. Hashimoto and R. Furuichi : The 79th Meting of Surf. Finish. Soc. Jpn, Mar., 1989.

Formation of Heat Resistant and Electron Conductive (La, Ca) CrO_3 Films by Electrodeposition ; H. Konno, M. Tokita and R. Furuichi : *ibid.*

Formation of Perovskite Structure Rare-Earth Chromium Oxides by Pyrolysis ; H. Konno, M. Tokita, S. Kitazaki and R. Furuichi: The 56th Ann. Meeting Electrochem. Soc. Jpn, Apr., 1989.

A New Apparatus Constructed for Acoustic Emission Thermal Analysis and Its Application to Thermal Decomposition of $KClO_4$; S. Shimada and R. Furuichi : The 58th Spring Meeting of Che. Soc. Jpn., Apr., 1989.

Surface Charge and the Point of Zero Charge of Metal Oxides ; H. Tamura, T. Oda and R. Furuichi : *ibid.*

Characterization of the Acid-Base and Ion Adsorption Behavior at Metal Oxide/Aqueous Solution Interfaces ; H. Tamura : The 8th Meeting of Radio-activity System Group of Jpn. Nucl. Ene. Ind. Council, Jun, 1989.

Field Assisted Dehydration of Hydroxide Films Formed at High

Temperature on Aluminum ; H. Takahashi and R. Furuichi : The 1989 Summer Meeting of Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. Anal. Chem. July, 1989.

Enhancement of the Activity of Sulfide Treated Mo/Al_2O_3 Catalysis by Evacuation at High Temperatures ; T. Katsuma, M. Sugioka, T. Kanazuka and H. Konno : *ibid.*

Studies on the Cobalt Complexes with Anomalous Electronic States (16). The Preparation and Properties of Paramagnetic Cobalt Complexes Having Oxine Derivative Ligands ; E. Toyota, Y. Yamamoto and H. Konno : The 39th Ann. Symp. on Coordination Chemistry, Sep., 1989.

A Role of Anions in the Formation of Hydroxide Films on Aluminum ; H. Takahashi, M. Yamaki and R. Furuichi : The 6th Intern. Symp. on Passivity, Sep., 1989.

Formation of Composite Oxide Films on Aluminum from Hydroxide Formed at High Temperature ; H. Takahashi, R. Furuichi and M. Nagayama : The 80th Meeting of Surf. Finish. Soc. Jpn., Oct., 1989.

Anodizing of Heat-treated Aluminum Die-cast Alloys in a Sulfuric Acid Solution ; K. Watanabe, H. Takahashi and R. Furuichi : *ibid.*

Formation of $La_{1-x}Sr_xCrO_3$ Films on Ni by Electrodeposition ; H. Konno, M. Tokita and R. Furuichi : *ibid.*

Effect of Anions on the Formation of Hydroxide Films on Aluminum during Hydrothermal Treatment ; H. Takahashi, M. Yamaki and R. Furuichi : The 36th Ann. Symp. on Corrs. and Protection, Oct., 1989.

Effect of $LaCrO_3$ Coating on the High Temperature Oxidation of Stainless Steels ; S. Kitazaki, H. Konno and R. Furuichi : *ibid.*

Composition of the Oxide Films on Fe-Cr Alloys Formed by Rapid High Temperature Oxidation ; H. Konno and R. Furuichi : *ibid.*

Observation of $ZnFe_2O_4$ Phase Formed on the Surface of Fe_2O_3 Prepared from Different Fe Compounds ; M. Ueda, S. Shimada and R. Furuichi : The 1989 Meeting of Hokkaido-Tohoku

Sec. Ceram. Soc. Jpn., Oct., 1989.

Characterization of the Acid-Base Properties of MnO_2 and Other Oxide Samples in Aqueous Media ; H. Tamura, M. Nagayama and R. Furuichi : The 4th Battery Mat. Symp., York, Oct., 1989.

Characterization of the Adsorption of Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} Ions on an MnO_2 Sample ; M. Nagayama, H. Tamura, N. Katayama and R. Furuichi : *ibid.*

A Study on the Thermal Decomposition of $KClO_4$ and $NaClO_4$ by Acoustic Emission Thermal Analysis ; S. Shimada and R. Furuichi : The 25th Meeting of Soc. Calorimetry and Therm. Anal. Jpn., Nov., 1989.

ELECTROMETALLURGY LABORATORY

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

Stndents

K. Miura, A. Hori, N. Yokoyama, S. Ando, T. Kumagai,
T. Mitsueda, Y. Shibata, G. Adachi, M. Maeda,
H. Sakashita, T. Yoshida and T. Yamamoto

Professor Ishikawa and Dr. Sasaki attended the 40th ISE Meeting held in Kyoto in Sep. 1989. Assoc. Prof. Narita attended the 2nd Intn. Symposium on High-Temperature Corrosion held in Le En-Bieze, France in May, 1989 and he visited Academy of Mining and Metallurgy, in Krakow, Poland in June 1989.

Dr. Notoya participated in the joint meeting of Australasian Corrosion Association Inc., Australasian Institute of Metal Finishing and Institute of Metals and Materials Australia "STEP INTO THE 90'S" Conference at the Gold Coast, Queensland from 27 to 31 August. He visited Dr. D. P. Schweinsberg at the Queensland University of Technology, Dr. H. Flitt at the Queensland Electricity Commission and Dr. G. Hope at Griffith University after the conference.

Dr. Sasaki returned to the laboratory in Sep. 1989 after one and a half years working with Professor D. A. Scherson at Case Western Reserve University, Cleveland, Ohio.

Researches in progress are as follows.

(1) Laboratory scale tests in bipolar electrode cells for electrowinning of liquid aluminum and its alloys containing titanium are being carried out by using alkali and alkali earth chlorides molten salts containing $AlCl_3$ and/or $TiCl_4$ in the temperature range from 700 to 800°C.

(2) Bipolar electrode cell developed for the aluminum electrowinning has been applied to obtain liquid magnesium from the chloride melt at 750°C.

(3) Sulfidation and reduction behavior of the preformed oxide scales on an Fe-25Cr-5Al and Fe-25Cr-5Al-Y alloys were investigated at 973 K in the H_2S-H_2 atmospheres.

(4) Ceramics-metal joinings: bonding systems investigated are as follows. Si_3N_4 and Fe-25Cr alloy with Ni-Cu-Ti filler, Al_2O_3 and Ni with Ag-Cu-Ti filler, and ZrO_2 and Cr with Ag-Cu-Ti filler.

(5) Corrosion and corrosion inhibition mechanisms of copper and its alloys have been studied with organic inhibitors by using electrochemical techniques. The influence of environment on an unusual type of corrosion in copper tubes in air-conditioning units have also been investigated.

(6) In relation with the corrosion of electronic circuits, electrochemical and spectroscopic studies on the corrosion of tin-lead alloys are in progress.

(7) In-situ spectroelectrochemical investigations on adsorbed molecules on various electrodes are also in progress.

(8) Measurement of residual stress on the ceramics joined to metals are being carried out using scanning acoustic microscopy which enables us to determine residual stress from changes in surface acoustic wave velocity.

Oral Presentation

The Effect of Yittrium Addition on the Break-down Behavior of Preformed Oxide Scale on Fe-Cr-Al Alloys by a H_2-H_2S Gas Mixture; T. Takahashi, T. Nairta and T. Ishikawa: The 24th Hokkaido Corrosion Seminar, Jan., 1989.

Preventive Measures for Preferential Dezincification of Betaphase in Commercial Brasses; T. Notoya, T. Ishikawa, T. Tsuji and Y. Watanabe: *ibid.*, Jan. 1989.

Changes in Fracture Strength of the YSZ/Metals Joints with Thermal Cycling Treatment: T. Narita, Y. Mizuta and T. Ishikawa: The 104 Spring Meeting of JIM, April, 1989.

Measurement of SAW Velocity on the Ceramics Joined to Metal using SAM; K. Miura, T. Narita and T. Ishikawa: *ibid.*, April, 1989.

Chemical Approach to Prevention of Dezincification in Commercial Brasses; T. Notoya, T. Ishikawa, T. Tsuji and Y. Watanabe: The 56th Spring Meeting of Japan Chemical Society, April, 1989.

Inhibition of Dezincification of Beta-Single Phase Brass by Organic Corrosion Inhibitors; T. Notoya and T. Ishikawa: The 104 Spring Meeting of JIM, April, 1989.

Evaluation of Corrosion Products by its Dissolution Behavior in Acidic Solution; S. Ohe, S. Konda, T. Narita and T. Ishikawa: The 56th annual Meeting Electrochem. Soc. of Japan, Apr., 1989.

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Stress Measurement with SAM; T. Narita: The Seminar on Ceramic/metal Joinings by JIM, June, 1989.

Topographical Classification of "Ant Nest Corrosion" in Copper Tubes; T. Notoya and T. Ishikawa: The 89' Hokkaido Section Spring Meeting of JIM, June, 1989.

Corrosion Inhibition Mechanism of Benzotriazole and Its Application to Copper Industries; T. Notoya: Corrosion Seminar at Japan Copper Development Association, June, 1989.

An Ant-Nest Corrosion in Copper Tubes Produced by HF Mist; T. Notoya and T. Ishikawa: The 1989 Summer Meeting of Hokkaido Section of Japan Chemical Society, July, 1989.

Unusual Type of Corrosion in Copper Tubes; T. Notoya, T. Ishikawa, T. Hamamoto and K. Kawano: STEP INTO THE 90'S Conference, August, 1989.

In-situ Infrared Spectroscopy as Applied to the Study of Molecules Irreversibly Adsorbed of Electrode Surfaces; T. Sasaki, I. T. Bae and D. A. Scherson: The 40th ISE Meeting, Sep., 1989.

Effect of Cell Wall Structures on the Performance of Bipolar Electrode Cell in Fused Chloride System; S. Konda, T. Narita and T. Ishikawa: The 40th ISE Meeting, Sep., 1989.

Characterization of Thin Si_3N_4 Film; Y. Abe, Y. Sakuta, Y. Yasozima and T. Narita: The 105th Autumn Meeting of JIM, Oct., 1989.

Joining of Stabilized Zirconia Ceramics to Metals; T. Mitsueda, T. Narita and T. Ishikawa, S. Nakamori and S. Hirai: *ibid.*, Oct., 1989.

Sulfidation Behavior of the Preoxidized Fe-25Cr-5Al Alloy in H_2-H_2S Atmospheres; H. Takahashi, T. Narita and T. Ishikawa: *ibid.*, Oct., 1989.

Evaluation of Residual Stress on the Ceramics Joined to Metals using SAM; K. Miura, T. Narita and T. Ishikawa: *ibid.*, Oct., 1989.

Measurement of SAW Velocity of Zirconia Ceramics; Y. Shibata, T. Narita and T. Ishikawa: *ibid.*, Oct., 1989.

The Effect of Adsorbed Tin on the Mode of Bonding of CO on Polycrystalline Platinum Electrode, an In-situ FTIRRAS Study; T. Sasaki, I. T. Bae and D. A. Scherson: The 176th Meeting of the Electrochemical Society, Oct., 1989.

Classification of Ant Nest Corrosion in Copper Tubes; T. Notoya and T. Hamamoto: The 29th Meeting of Japan Copper and Brass Research Association, November, 1989.

Electrowinning of High-pure Metals by an Electrochemical Cycle in Molten Salt System. (Part 1) Introduction of Electrochemical Cycyle for Energy Saving; T. Ishikawa: The 21st Symposium on Molten Salt Chemistry, Nov., 1989.

Electrowinning of High-pure Metals by an Electrochemical Cycle in Molten Salt System. (Part 2) Possibility of Aluminum-Chlorine Fuell Cell; S. Ando, S. Konda, T. Narita and T. Ishikawa: *ibid.*, Nov., 1989.

Electrochemical Formation of Intermetallic Compound Al_3Ti in the Chloride Melt Containing $TiCl_4$; T. Kumagai, S. Konda, T. Narita and T. Ishikawa: The Hokkaido Section Fall Meeting of JIM, Nov., 1989.

Toward a More Fundamental Understanding of Corrosion Processes

Norio Sato

Corrosion, **45**, No. 5, p. 354–368 (1989)

A review is given of some simplified concepts that will contribute to a better understanding of corrosion fundamentals. The corrosion process involves not only electrochemical reactions but also acid-base reactions, and it is the acid-base nature that diversifies the corrosion phenomena. Anions either catalyze or inhibit the anodic metal dissolution, and the passivation will result from the hydroxide-catalyzed mechanism of metal dissolution. Corrosion precipitates frequently control the selective mass transport in corrosion processes. Anion-selective precipitates accelerate and cation-selective precipitates decelerate corrosion propagation. A bipolar precipitate film, if anodically polarized, undergoes deprotonation and turns into a passive film. The electrochemical stability of passivated metals is determined by the electron energy band structure of the passive film. The passive film of n-type semiconducting oxides appears electrochemically more stable than the passive film of p-type semiconducting oxides. (English)

Piezoelectric Detection of Interfacial Change of Gold Electrode in Relation to Underpotential Deposition of Copper

Masahiro Seo, Xiang Chun Jiang and Norio Sato

Electrochimica Acta, **43**, No. 8, p. 1157-1158 (1989)

A piezoelectric detection of surface stress change of solid electrode produced by an electromodulation was attempted to investigate the shift in potential of zero (pzc) of gold electrode with relation to underpotential deposition of copper in sulfuric acid solution. The relation between shift in pzc, ΔE_p and surface coverage of copper, θ drew a sinusoidal shape with a critical point of about $\theta=0.42$ at which surface reconstruction or rearrangement would take place. (English)

In-situ Analysis of Chloride Ion Concentration within Pits during Pitting of Iron

Tadahiko Mizuno

Passivity of Metals
Proceedings of the Sixth International Symposium on Passivity-Part I
Passivation of Metals and Semiconductors, Sapporo, Japan 24-28 September 1989, Pergamon Press (1990), 497-502

Pitting corrosion of pire iron in borate buffer solution was studied by in-situ measurement of chloride isotope ^{36}Cl. Relationships between concentration of chloride ions and current density in a pit during pitting corrosion are discussed. (English)

Application of the Electrochemical Test Method for Copper Tubes (BNF Rapid Test) to Evaluate Pitting Propensity of Wateers and Its Limitations

Takenori Notoya

Bulletin of the Faculty of Engineering,
Hokkaido University. No. 146 (1989)

Evaluation of pitting corrosion propensity of supply waters was made by use of the BNF electrochemical cell which was developed by British Non-Ferrous Technology Centre to determine the water capability to support Type I pitting in copper tubes. Twenty five different waters tested include tap waters, natural well waters, artificial waters having different chemical compositions and dilute NaCl solutions in the presence of organic corrosion inhibitors for copper. The cell assembly, condition of operation, interpretation of the results, advantages and shortcomings of the BNF cell are described. The common types of pitting corrosion in copper tubes were classified. Feasibility of the BNF cell application was examined to waters prone to Type II pitting which is most prevalent type of pitting corrosion in Japan. It was concluded that the BNF cell showed the pitting propensity of waters suceptible to Type I pitting but it was not sensitive for those of Type II pitting. It is suggested that morphology and coverage of corrosion products formed on the center and surrounding anode elements in the BNF cell determine the water corrosive aggressivenss in copper tubes. (Japanese)

Inhibition of Dezincification of Commercial Brass by Organic Inhibitors

T. Notoya

Journal of the Japan Copper and Brass Research Association Vol. 28 p. 27 (1989)

Inhibition action of seven organic chemicals as dezincification inhibitors for six different commercial brasses was investigated using a potentiostatic acceleration technique in an acidified and a neutral 0.5 M NaCl solutions at 60°C. Brasses used were two dezincification resistant brasses of both TCA (α single phase) and NFS (9% β phase), C3604 (14%) free cutting brass, C4641 (22%) naval brass, C3771 (27%) forging brass and C6782 (62%) high strength brass. Among seven organic inhibitors benzotriazole, tolyltriazole and phenyl triazine dithiol were found to be effective in inhibiting anodic dissolution of copper and zinc from the brasses in the solutions. It was concluded that dezincification attack in the brasses can be prevented by addition of small amount (ca. 1 mM) of these inhibitors to corrosive environments. (Japanese)

Formicary Corrosion in Copper Tubes in Wet Atmospheric Conditions

Takenori Notoya, Takao Hamamoto
and Kozo Kawano

Sumitomo Light Metal Technical Reports
Vol. 30, No. 3 p. 123 (1989)

Uniform oxidation is the most common type of corrosion of copper tubes in refrigerating and air-conditioning units. Recently an unusual type of corrosion, "Formicary corrosion", has been reported in such copper tubes at the final leakage test before shipment of those units or in the extremely short running after installation. The corrosion is characterized by complicated microscopic caverns of porous copper oxide connected by tunnels. The microcaverns have voids and microcracks and the surface of the copper tubes is tarnished greyish-brown or blue-violet without bulky corrosion products and shows no obvious defects indicating the leaks. Twenty one cases of such premature failures of copper tubes discovered during the four years from 1984 to 1987 are shown in Table 1. In a few cases carboxylic acids may have been the corrosive media, because formic and acetic acids were detected in the atomosphere where the copper tubes were placed. Experiments produced similar corrosion after copper tubes were exposed to a humid oxygen atmosphere with small amounts of carboxylic acids for a few months. The carboxylic acids were formic acid, acetic acid, propionic acid, and n-butyric acid. The mechanisms of propagation of the corrosion and preventive measures are presented. (Japanese)

Unusual Corrosion in Copper Tubes

T. Notoya, T. Ishikawa, T. Hamamoto
and K. Kawano

Transaction of STEP INTO THE 90'S
Conference Vol. 2 p. 565 (1989)

Uniform oxidation is the most common type of corrosion of copper tubes in refrigerating and air-conditioning units. Recently an unusual type of corrosion' "Formicary corrosion", has been reported in such copper tubes during leakage tests after manufacture or after short periods of use. The corrosion is characterized by complicated microscopic caverns of porous copper oxide connected by tunnels. The microcaverns have voids and microcracks and the surface of the copper tubes is tarnished greyish-brown or blue-violet with bulky corrosion products and shows no obvious defects indicating the leaks. Twenty one cases of such premature failures of copper tubes discovered during the four years from 1984 to 1987 are shown in Table 1. In a few cases carboxylic acids may have been the corrosive media, because formic and acetic acids were detected in the atomosphere where the copper tubes were placed. Experiments produced similar corrosion after copper tubes were exposed to a humid oxygen atmosphere with small amounts of carboxylic acids for a few months. The carboxylic acids were formic acid, acetic acid, propionic acid, and n-butyric acid. The mechanisms of propagation of the corrosion and preventive measures are presented. (English)

Radiation Effects on Volumetric Change and Corrosion for Simulated Radioactive Waste Glass

S. Sato, Y. Inagaki, H. Furuya and T. Tamai

Proceedings of the 1989 Joint International Waste
Management Conference Vol. 2, p. 323-328
Kyoto JAPAN, Oct. 22-28 (1989)

Simulated radioactive waste glasses were irradiated, using three kinds of facilities: a high-voltage electron microscope, an electron accelerator, and a nuclear reactor. Radiation effects on microstructural change, density change, annealing properties of the density change, and leaching properties were studied by the authors and are reviewed in this paper.

Waste glass swelled or shrank at most 0.6%, depending on the kind of glass when irradiated in a nuclear reactor with $^{10}B(n,\alpha)^7Li$ reaction up to a fluence of 6.6×10^{25} reaction/m^3. Helium bubble was observed in the irradiated glass. The cumulative irradiation is roughly equivalent to irradiation during a few tens of thousand years after disposal. The irradiated waste glasses swelled at most 0.5% when thermally annealed above the temperature of 620K. The glass which shrank as the result of the (n,α) irradiation swelled larger than glass which swelled.

The apparent diffusion coefficient of Cs obtained from normalized elemental mass loss of Cs decreased an order of magnitude when irradiated with the reaction beyond around 0.1 dpa (displacements per atom). (English)

Inhibition in Context of Passivation

Masahiro Seo and Norio Sato

Corrosion/89, NACE, Paper No. 138, p. 1-18 (1989)

This article deals with anodic dissolution and passivation of metals in relation to anodic inhibiton of metallic corrosion. It is stressed that an adsorption of electrolyte ions on the metal surface plays vital roles in the anodic dissolution and passivation of metals. In particular, it is pointed out that the acid-base nature of metal's surface or metal ions and ligands, is one of the important factors which controls the chemical stability of adsorption intermediates and metal-hydrated complex ions in solution. Furthermore, the roles of passivators in corrosion inhibition are discussed from the viewpoint of not only adsorption but also the ion-selectivity of corrosion precipitate films. (English)

Vibrational Spectroscopic Study of Structural Evolution in the Coprecipitated Precursors to $La_2Sn_2O_7$ and $La_2Ti_2O_7$

Junichi Takahashi and Toshiaki Ohtsuka

J. Am. Ceram. Soc., **72**. 426 (1989)

Structural evolution in the X-ray amorphous precursors to $La_2Sn_2O_7$ and $La_2Ti_2O_7$ is examined using IR and Raman spectroscopy. These precursors are prepared by rapid coprecipitation from mixed aqueous solutions of the corresponding metal chlorides. Rapid coprecipitation from an $SnCl_6^{2-}$ and La^{3+}-containing aqueous solution yields microcrystalline particles of $SnO_2 \cdot nH_2O$ and $La(OH)_3$, which instantaneously interconnect to form an ultimate, complex colloid particle. The $Ti(OH)_2^{2+}$ and La^{3+} in the other solution system coprecipitate into a different, complex colloid (an unidentified phase), which is definitely not a mixed dispersion of single-component colloids. A comparative examination of the vibrational spectra of the coprecipitates heated to various temperatures indicates that the SnO_2 and anatase phases develop in the respective precursors before crystallization of the desired double oxide. Crystallization itself can be attributed to a solid-state reaction among the various microcrystallites of each single-metal oxide in a gel particle of the precursor. (English)

Laser Raman Spectroscopy

Toshiaki Ohtsuka

The Journal of the Surface Finishing Soc.
of Japan, **40**, 1000 (1989)

Due to the recent advance of Laser technology and light detection technique, the Raman spectroscopy can be widely used for the observation of solid surfaces. The application to the solid surface was introduced on following topics ; 1) Sensitivity of Raman spectroscopy to the surface thin layer, 2) In-situ Raman spectra from the anodic oxide films, 3) SERS spectra of NiOOH layer deposited on Ag, 4) Raman mapping of corrosion product formed on stainless steel, and 5) Electronic Raman spectra of semiconductor surface. (Japanese)

Characterization of the Adsorption Behavior of Copper (II) Ions on the Surface of Manganese-Dioxide Particles

Hiroki Tamura, Taro Tatsumi
and Ryusaburo Furuichi

Hyomen Gijutsu, **40**, 1116–1120 (1989)

The adsorption of Cu^{2+} ions on MnO_2 was examined as a function of pH and concentrations of Cu^{2+} and MnO_2. The adsorption isotherm shows that the surface concentration of adsorbed Cu^{2+} increases with pH and concentration of Cu^{2+} in solution, and that, at higher coverages, the surface concentration is lower than predicted by the Langmuir isotherm. The behavior was characterized by considering the stoichiometry and equilibrium and concentration conditions of the adsorption. The surface acid hydroxyl groups, $\equiv MnOH(a)$, react with Cu^{2+} ions to form the following two surface complexes: $\equiv MnOH(a) + Cu^{2+} + NO_3^- \rightleftarrows \equiv MnOCu^+ \cdot NO_3^- + H^+$, $2\equiv MnOH(a) + Cu^{2+} \rightleftarrows (\equiv MnO)_2Cu + 2H^+$. The equilibrium conditions of these surface complexations are given by: $K_1^{\mathrm{int}} = Q_1^{\mathrm{eq}} \exp(B_1 [\equiv MnOCu^+ \cdot NO_3^-])$, $\beta_2^{\mathrm{int}} = Q_2^{\mathrm{eq}} \exp(B_2 [(\equiv MnO)_2Cu])$, where K_1^{int} and β_2^{int} are "intrinsic" stability constants of (1 : 1) and (1 : 2) surface complexes, Q_1^{eq} and Q_2^{eq} are concentration quotients at equilibrium, and B_1 and B_2 are constants expressing the extent of suppression of surface complexation by the respective complexes. The equations of equilibrium conditions and of concentration conditions for both solution and surface species were fitted to the adsorption isotherm, and the values of the constants were determined by the nonlinear least-squares method. The values are: $K_1^{\mathrm{int}} = 8.15 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}}$, $\beta_2^{\mathrm{int}} = 2.41 \times 10^3\ \mathrm{m^{-1}}$, $B_1 = 3.81 \times 10^6\ \mathrm{m^2\ mol^{-1}}$, and $B_2 = 1.62 \times 10^6\ \mathrm{m^2\ mol^{-1}}$ at an ionic strength of 0.1 ($NaNO_3$) and 25°C. These values well describe the observed adsorption behavior. (Japanese)

Acid-Base Dissociation of Surface Hydroxyl Groups on Manganese Dioxide in Aqueous Solutions

Hiroki Tamura, Tatsuya Oda, Masaichi Nagayama
and Ryusaburo Furuichi

J. Electrochem. Soc., **136**, 2782–2786 (1989)

The surface charge on MnO_2 in $NaNO_3$ solutions was measured as a function of pH and ionic strength by titration. With increasing pH, the surface charge changed from positive to negative through zero at a certain pH (PZC). The absolute value of the charge increased with increasing ionic strength. The surface charge was interpreted in terms of the dissociation of acid and base surface hydroxyl groups on MnO_2, that is an ion exchange: $\equiv MnOH(a) + Na^+ \rightleftarrows \equiv MnO^- \cdot Na^+ + H^+$, $\equiv MnOH(b) + H_2O + NO_3^- \rightleftarrows \equiv MnOH_2^+ \cdot NO_3^- + OH^-$. The charged sites adsorb counterions electrostatically. The equilibrium conditions of these reactions were derived by considering a suppression of dissociation by the formed charged sites: $K_a = [\equiv MnO^- \cdot Na^+][H^+] \exp(A_a[\equiv MnO^- \cdot Na^+])/([\equiv MnOH(a)][Na^+])$, $K_b = [\equiv MnOH_2^+ \cdot NO_3^-][OH^-] \exp(A_b[\equiv MnOH_2^+ \cdot NO_3^-])/([\equiv MnOH(b)][NO_3^-])$, where K_a and K_b are acid-base dissociation constants and A_a and A_b are constants expressing the suppression of dissociation by the charged sites. The relationship between the surface charge, pH, and ionic strength was analyzed by a nonlinear least squares method with equations for the equilibrium and concentration conditions, and values for the constants were established. The suspension pH and point of zero charge of MnO_2 were derived as a function of these constants and they were consistent with the measured values. (English)

Anodizing of Aluminum Covered with Hydroxide Films
III. Effect of Anodizing Temperature on the Void Distribution in the Composite Oxide Film

Hideaki Takahashi, Yasutoshi Umehara,
Ryusaburo Furuichi and Masaichi Nagayama

J. Surf. Finish. Soc. Jpn., **40**, 590–597 (1989)

Hydroxide were formed on aluminum specimens by immersing them in water at temperature (T_b) of 100–180°C, and the specimens were then anodized galvanostatically in a neutral borate solution to form composite oxide films. The formation behavior of the hydroxide and composite oxide was followed by gravimetry, X-ray photoelectron spectroscopy, electron microscopy, and electric capacitance measurements.

It was found that the growth rate of the hydroxide films increased with increasing T_b, and that the hydroxide/metal interface roughened increasingly due to the non-uniform growth of the hydroxide. The water content of the hydroxide (value of X in $Al_2O_3 \cdot XH_2O$) decreased from 2.7 to 1.8 when T_b increased from 100 to 180°C.

The composite oxide films that formed after boiling at different values of T_bs were all composed of an outer crystalline oxide layer (thickness δ_o) and an inner amorphous oxide layer (thickness δ_i), and while δ_o did not depend on T_b, δ_i decreased with increasing T_b. The composite oxide films formed by anodizing to $E_a = 300$ V showed thickness/voltage ratios ($(\delta_0 + \delta_i)/E_a$) of only 1.10 to 0.87nm/V, decreasing with increasing T_b. The capacitance and dielectric loss of the composite oxide films increased with T_b.

The effect of T_b on the formation behavior of composite oxide films is discussed by considering the volume changes caused by the field-assisted dehydration of hydroxide to form a barrier oxide layer. (Japanese)

Anodizing of Aluminum Covered with Hydroxide.
IV. Field Assisted Dehydration of Hydroxide Formed in High Temperature

Hideaki Takahashi, Kazuo Takahashi,
Ryusaburo Furuichi and Masaichi Nagayama

J. Surf. Finish. Soc. Jpn., **40**, 1415-1421 (1989)

Composite oxide films were formed anodically on hydroxide-covered aluminum in a boric acid/borate solution at 40, 60, 80, and 95°C, and then relaxed by allowing water to penetrate into the voids in the oxide films. After relaxation, specimens were re-anodized with a low current to measure the time-variation in the anode potential, E_{ref}. The void distribution in the composite oxide films was determined by analyzing the E_{ref} vs. t_{ref} curve.

It was found that the penetration of water started after an induction period, and that the apparent activation energy for the relaxation of composite oxide films was 69.5 KJ/mol. Voids were observed in high concentrations at the inner layer/outer layer interphase, and at the center of the outer layer in the composite oxide film. The total volume of voids increased with anode potential, E_a, during anodizing at all temperatures except 95°C; at 95°C, the void volume increased with E_a up to $E_a = 300$ V, and then decreased to a small value at $E_a = 400$ V. The void volume showed a maximum at 60°C for all values of E_a.

Film formation mechanisms are discussed to explain how void distribution is established. (Japanese)

Electrochemical Formation of Lanthanum Chromite Coatings

Hidetaka Konno, Masahiro Tokita,
Satoru Kitazaki and Ryusaburo Furuichi

J. Surf. Finish. Soc. Jpn., **40**, 144 (1989)

A novel method of the formation of lanthanum chromite, $LaCrO_3$, films on metals were developed utilizing cathodic deposition from chromate solutions containing lanthanum ions. (Accelerated Communication) (Japanese)

Perovskite Structure Lanthanum Chromium Oxide Film Formation Employing Electrodeposition

Hidetaka Konno, Masahiro Tokita,
Satoru Kitazaki and Ryusaburo Furuichi

J. Surf. Finish. Soc. Jpn., **40**, 825 (1989)

A method to form $LaCrO_3$ oxide films on metals was developed. It was found that cathodic polarization of metals in La(III)-Cr(VI) solutions forms La(III)-Cr(VI) oxyhydroxide films on the metals. By controlling solution composition and pH, cathode potential, and electrolysis time, $LaOH(CrO_4)xH_2O$ films were obtained with good reproducibility. The compound was found to decompose to $LaCrO_3$ at lower temperatures and with shorter pyrolysis times than La(III) and Cr(III) compound precursors. The $LaCrO_3$ film on stainless steels displayed good oxidation resistance. The $LaCrO_3$ powder can also be synthesized from La(III)-Cr(VI) systems with lower energy consumption. (Japanese)

Surface Oxidation of Alloys —Behaviors in the Relatively Low Temperature Region—

Masahiro Seo

J. Surf. Sci. Soc. Japan, **10**, No. 9,
p. 558-564 (1989)

This article reviews surface oxidation behaviors of alloys in the relatively low temperature region less than 800 K, particularly focussed on the selective oxidation of iron base- and nickel base-alloys. In general, the selective oxidation starts with the alloying element with higher affinity to oxygen, followed by the subsequent oxidation of the remaining elements with lower affinity to oxygen. It was stressed that the interdiffiusion process of substrate alloy was one of the important factors controlling the selective oxidation of the alloys. (Japanese)

Internal Sulphidation Phenomena of Heat-resistant Alloys at Low Sulphur Pressures

Toshio Narita and Tatsuo Ishikawa

Materials Science and Engineering,
A 120 (1989) 31-38

Three types of internal sulphidation (general internal, integranular) and a mixture of these occured beneath relatively thick surface scales at low sulphur pressures where a noble metal sulphide is unstable. This critical sulphur pressure was higher when the surface sulphide scales were highly protective, as observed for Fe-Cr-Al and Fe-Mn alloys sulphidized at intermediate sulphur pressures.

Copious internal sulphidation was formed by sulphidation of Fe-Mn, Fe-Ni and Ni-Cr alloys. For an Fe-26.6%Cr alloy the internal sulphidation occurred at 1173 K while it was confined along the grain boundaries at 1073 K. With increasing chromium content, a mixture of internal and intergranular sulphidation was formed at both temperatures.

Austenitic stainless steels, SUS 316L and Incoloy 800, formed copious internal sulphidation at sulphur pressures of $10^{-3.5}$ and 10^{-3} Pa, and with decreasing sulphur pressures this changed rapidly to intergranular sulphidation.

The usual internal sulphidation is explained by assuming an enhanced diffusion flux of sulphur due to the sulphur-metal interaction in the alloy phase, which has very low chemical diffusivity. For alloys with relatively high chemical diffusivity intergranular sulphidation takes place, because the metal-scale interface is unstable and the grain boundaries become inward protruding sites. (English)

Metallization on the Surface of a SiC Ceramics by Using Cr Vapor

Toshiyuki Takashima, Tsuyoshi Yamamoto
and Toshio Narita

J. Ceram. Soc. Jpn. Inter. Ed.
Vol. 97 [36-40] (1989)

Formation of Cr-metallied layer on the surface of SiC ceramics by the vapor-diffusion method was studied. The metallization was carried out at 1273 K up to 360 ks in a evacuated chamber. As a vapor source, pure Cr powder was used. The kinetics of layer growth was described by the parabolic law with the rate constant of 4.2×10^{-16} m²/s at 1273 K. The metallized layer was composed of four layers; fouble carbide: $Cr_{5-X}Si_{3-Z}C_{X+Z}$ at the bottom layer, chromium silicide: Cr_5Si_3 at the middle layer, a transition layer from chromium silicide to chromium carbides which consist of a Cr_7C_3 and Cr_3C_2 at the surface layer. (English)

Effect of Cell Wall Structures on the Performance of Bipolar Electrode Cell in Fused Chloride System

Shoichi Konda, Toshio Marita
and Tatsuo Ishikawa

Proceddings of the 40th ISE, 1 (1989), p. 90.

In order to operate effectively the bipolar cell, it can not be adopted freezing formation technique of the melt between an inner wall and the bipolar electrode, because it is prerequisite to keep a wall-designed clearance in the periphry part of the cell for smooth circulating of the electrolytic melt.

The authors have been experimentally confirmed anti-corrosive properties of a recrystallized alumina tile as the most inner wall to the chloride melt, devised newly particles-packed wall as an intermediate wall structure and measured the thermal condactivity of such composited cell wall.

According to these experimental results, the author devised further more reasonable wall structure of tubes-stacked type. In this type of the wall structure, a great number of one-end sealed tubes are regulary stacked to make the intermediate cell wall.

In this study, electrolytic experiments of five units bipolar electrode cell with quartz tubes-stacked wall were carried out and decrements of the cell efficiencies owing to the permeated melt in the wall were evaluated from the linear relations between applied currents and bath voltages. It can be clarified some promising properties of the tubes-stacked structure as the cell wall for the industrial bipolar cell. (English)

Cold Fusion — Are There Any Unknown Reactions in Metal Hydrogen System ?

T. Mizuno, T. Akimoto and N. Sato

J. Heat Transfer Soc. Japan, Vol. 28,
No. 111, (1989) 23-32

The details of discovery and present condition of cold fusion were described. A point of issue, the mechanism and possibility for the use of the cold fusion as an energy source were discussed. The reasons of the difficulty of confirmation of the cold fusion and low reproducibility of the reaction were considered with some speculation for the mechanism. The expectation for use of the cold fusion reaction as an energy source was suggested. (Japanese)

Possibility of Cold Fusion

T. Mizuno

Expectation Series for Technics Vo. 6,
No. 24 (1989) 249-255

The circumstances of discovery and present conditions of cold fusion study were described. The mechanism of the reaction and the possibility for use of as an energy source were discussed. The reasons of the difficulty of confirmation of the cold fusion and low reproducibility of the reaction were considered with some speculation for the mechanism. The crack mechanism is shown as one of the most suitable model, and explains the situation of the cold fusion. The expectation for the practical use of the cold fusion reaction as an energy source was suggested. (Japanese)

Examination and Theory of Cold Fusion Which Shook the Scientific World

T. Mizuno

The Newest Scientific Essay, Series 9, The Newest
Study of Nuclear Energy (1990) 26-32

The circumstances of discovery and present conditions of cold fusion study were described. The mechanism of the reaction and a possibility for the use as an energy source were discussed. The reasons that the difficulty of confirmation of the cold fusion and low reproducibility of the reaction were considered with some speculation for the mechanism. The crack mechanism seems to be one of the most suitable model, and explains the situation of the cold fusion. And the validity of the mechanism of the cold fusion reaction was discussed with the measurement result obtained by a deuteron accelerator. The expectation for the practical use of the cold fusion reaction as an energy source was suggested. If the crack mechanism can be taken a proper model to the cold fusion, neutron evolution for an ideal condition should be increased by $10^8 \sim 10^9$ orders of magnitude. At the same case, we could get the heat of $10^{-4} \sim 10^{-3}$ Joule/s/kg for the metal absorbed hydrogen. (Japanese)

Neutron Detection and the Mechanism of the Cold Fusion

T. Mizuno, T. Akimoto and N. Sato

Genshikaku Kenkyu Vol. 34, No. 3, (1990) 47-54

The validity of the crack mechanism for the cold fusion was considered on some measurements which have been obtained by a deuteron accelerator. If the crack mechanism can be assumed as a proper model of the cold fusion, neutron evolution for an ideal case should be increased by $10^8 \sim 10^9$ orders of magnitude. (Japanese)

Neutron Evolution from Pd Cathode Electrode in LiOD-D_2O Solution

T. Mizuno, T. Akimoto and N. Sato

Nuclear Fusion Reactor (A special number for
Cold Fusion) Vol. 22, (1989) Sept., 15-16

The experimental details and the results were described. Neutron energy spectra obtained from a cathodically polarized Pd and after electrolysis in LiOD-D_2O solution were shown. It may be concluded that the d-d nuclear fusion reaction takes place in or on the Pd electrode during cathodic charging. (Japanese)

Cold Fusion (A Consideration on the Mechanism)

T. Mizuno, T. Akimoto and N. Sato

J. Surface Sci. Soc. Jap., Vol. 10,
No. 9 (1989) 602-605

The details of discovery and present condition of cold fusion were described. A point of issue, the mechanism and a possibility for the use of the cold fusion as an energy source were discussed. The reasons of the difficulty of confirmation of the cold fusion and low reproducibility of the reaction were considered with some speculation for the mechanism. (Japanese)

Neutron Evolution from Annealed Palladium Cathode in LiOD-D_2O Solution

Tadahiko Mizuno, Tadashi Akimoto
and Norio Sato

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In response to the reports of cold fusion in the electrolysis of D_2O, we examined the evolution of neutrons from a palladium electrode being cathodically charged in LiOD-D_2O solution. The evolution of 2.5 MeV neutrons which correspond to one of the reaction products of nuclear fusion were observed during electrolysis. It may be concluded that the d-d nuclear fusion reaction takes place in or on the Pd electrode during cathodic charging. We could estimate the rate of neutron production of d-d fusion during electrolysis; it was almost same to the value obtained by Jones et al. (English)