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The research activities of the laboratory are mainly concerned with a chemical cell, electrorefining of Al, and surface finishing in molten salts, and also with corrosion phenomena in aqueous and atmospheric environments, and mechanisms of inhibitors.

Current topics on research are in the following:

(1) Electrochemical cycle system for production of aluminum from scrap aluminum.
An Al-Cl_2 chemical cell, one component step of the electrochemical cycle system, has been investigated focusing an effective three-phase reaction zone. In order to evaluate the function of cathodes for the reduction reaction of chlorine gas to chloride ions, several cathodes with various types of a three-phase reaction zone were tested in chloride melts containing $AlCl_3$ at about 750° C.The other component steps of the system are also under investigation.

(2) Electrorefining of Al from scrap aluminum in a bipolar electrode system.
For electrorefining of Al from scrap aluminum by using a bipolar elec-

trode system, an available molten salt predominantly composed of chloride was developed. The anodic dissolution characteristics of Al-Cu alloys and the dependency of cathodic polarization curves on concentrations of AlF_3 have been investigated in the melts together with the effect of cell materials on the reaction.

(3) Co-depositon of Ti and Al in a low temperature molten salt.

The electrochemical characteristics together with the morphology are being studied in co-deposition of titanium with aluminum in chloride melts containing $AlCl_3$ at 200℃. By electrolysis, first, an aluminum deposition took place and it was followed by a reaction of the deposited aluminum with $TiCl_4$ forming Ti-Al layers. The Ti content of a 30 mass% was achieved.

(4) Corrosion test of iron covered with an electrodeposited Al layer.

Corrosion behavior of iron covered with an aluminum layer electrodeposited from room-temperature molten salt baths is being investigated in tap water and the dependency of corrosion potential on the ratio of covered areas with aluminum to bare surface areas of substrates is also being monitored.

(5) Corrosion behavior of tin-lead alloys in an aqueous environment.

In relation to the corrosion of electronic circuits, electrochemical investigations of several compositions of tin-lead alloys in dilute sulfuric acids are in progress. The quantities of corrosion of both components of the alloys in the solution and corrosion layers were determined respectively. The effect of chloride ions on their corrosion rates is also under investigation.

(6) Surface layers initially formed on metals in gaseous corrosion environments.

Surface layers initially produced on copper and iron in nitrogen or air containing sulfur dioxide and water vapor are being investigated by in situ techniques, such as IR-RAS and QCM. An in situ technique composed of combined IR-RAS and QCM has been developed. Applying the technique to investigation of surface layers formed on copper in air with SO_2 and water vapor, the thickness of sulfite and water layers on copper specimens was determined.

(7) Inhibitors.
The mechanisms of inhibition action of newly-developed benzotriazole derivatives were studied for copper and copper alloys using electrochemical and SERS techniques. Unusual localized corrosion, Ant's Nest Corrosion, in copper tubes was also studied under simulated conditions to understand its mechanism and to prevent this mode of corrosion in thin-walled copper tubes

(8) Concrete corrosion
Research effort has been focused to prevent steel bar corrosion in steel fiber reinforced concrete for corrosion protection of reinforced concrete structures and for making use of waste steel cans.

Other activities:
Prof. T. Ishikawa and Mr. M. Ueda attended the 10th International Symposium on Molten Salts which was held in Los Angels, California, USA, in May and presented a paper entitled "Characteristics of cathodic reaction in $BaCl_2$-NaCl melts containing AlF_3 components". Afterward they visited the Los Alamos Laboratory in Los Alamos, New Mexico, USA.

Assoc. Prof. T. Sasaki participated in the 190th Electrochemical Society Meeting, San Antonio, Texas, USA in September and presented a paper entitled "IR-RAS and QCM as Combined in situ Probes of an Initial Corrosion Layer of Copper in a Corrosive Gas Environment".

Assoc. Prof. T. Sasaki and Lecturer T. Notoya took part in the 13th International Corrosion Congress in Melbourne, Australia, in November.

Presentations

Measurement of Electrical Conductivity in a $BaCl_2$-NaCl-AlF_3-NaF System; M. Ueda, S.Konda, T. Sasaki and T. Ishikawa: The Joint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn, Surf. Finish. Soc. Jpn, and Jpn. Soc. Corros. Eng. Sapporo, Jan., 1996.

IR-RAS of Corrosion Products; J. Itoh, T. Sasaki and T. Ishikawa: ibid.

On Adsorption of Anions and Capacity of Electric Double Layer at a Polycrystaline Gold / Electrolyte Interface; S. Hara, T. Sasaki and T. Ishikawa: ibid.

In situ Measurement with FT-IRAS and QCM of Corrosion Layers Initially Formed in Atmosphere; T. Sasaki, T. Itoh, J. Itoh, and T. Ishikawa: ibid.

Codeposion of Al and Ti in Low Temperature Melts Containing AlCl3; N. Ohya, S. Konda, T. Sasaki and T. Ishikawa: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn. Sapporo, Jan., 1996.

Corrosion Resistivity of Various Carbon Materials as an Anode of Chlorine Cell in Low Temperature Melts Containing $AlCl_3$; S. Konda, T. Sasaki and T. Ishikawa: ibid.

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SERS Spectrum of Benzotriazole Related Compounds on Copper Electrode in Sulfuric Acid ; T.Notoya,A.R.Truman & D.P.Schweinsberg:The 70th Spring Meeting of Jpn. Chem.Soc.,Tokyo,March,1996.

In situ Measurement of Corrosion Layers Initially Formed on Copper in Air Containing SO_2 and H_2O; T. Itoh, T. Sasaki and T. Ishikawa: ibid.

Dependency of Bath Voltage on Inter-electrode Distances in Chloride Melts Containing 40 mol% AlF_3-NaF; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: The 63rd Annual Meeting of Electrochem. Soc. Jpn., "Properties of Molten Salts and Its Application", Koganei, April, 1996.

Al-Cl_2 Chemical Cell in Chloride Melts Containing $AlCl_3$; S. Konda, K. Imasawa, T. Sasaki and T. Ishikawa: ibid..

Characteristics of Cathodic Reaction in $BaCl_2$-NaCl Melts Containing AlF_3 Components; M. Ueda, S. Konda, T. Sasaki and T. Ishikawa: 10th Int. Symp. Molten Salts, Los Angels, May, 1996.

In situ IRAS-QCM Investigation of Thin Water Layer Formed on Gold; J. Itoh, T. Sasaki, M. Seo and T. Ishikawa: Corrosion '96 of Jpn. Soc. Corros. Eng., Tokyo, May 1996.

Corrosion Layer Initially Formed on Iron in a Corrosion Environment Containing SO_2 and H_2O; T. Sasaki, T. Miyano and T. Ishikawa: ibid.

Simulation of Protection Performance of Steel Fibers in Reinforced Concrete Members ;A.Keyvani Someh,N.Saeki & T.Notoya:The 50th Cement Technology Meeting, Tokyo, May, 1996.

In situ IR-RAS and QCM Measurement of Copper Surfaces; J. Itoh, T. Sasaki, M. Seo andT. Ishikawa: The Summer Joint Meeting of The Hokkaido Secs. of Jpn, Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, July, 1996.

In situ IR-RAS Measurement of Surface Layers on Iron Containing Copper; T. Sasaki, T. Miyano and T. Ishikawa: ibid.

Synergistic Effect of Benzotriazole Derivatives and Potassium Iodide on CopperDissolution in Sulfuric Acid Solution; T.Notoya & D.P.Schweinsberg :The 1996 Summer Meeting of the Hokkaido Section of Jpn. Chem. Soc., July,Asahikawa,1996.

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Scholarships to Overseas Students at Department of Engineering, Hokkaido University; T.Notoya: JIM'96 Fall Annual Meeting(119th),Sapporo,September, 1996.

Benzotriazole Treatment of Copper Wire by High Pressure Water Jet:Part 2 ; T. Tomitsuka,N.Tanabe & T.Notoya:JIM'96 Fall Annual Meeting(119th), Sapporo, September, 1996.

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Corrosion Inhibition Action of Benzotriazole Derivatives on Corrosion of Copper in Sulfuric Acid Solution ; T.Notoya :The 36th Meeting of Japan Copper and Brass Research Association, Tokyo, November, 1996.

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Corrosion Protection of Steel Reinforced Concrete Members by Using Recycled Steel ; A.Keyvanni Someh, N.Saeki & T.Notoya:The 12th

International Conference on Solid Waste Technology and Management,Philadelphia,PA,USA,November, 1996.

In situ IR-RAS Investigation of Surface Layers Initially Formed on Copper and Low Carbon Steel in Nitrogen or Air Containing Water Vapor and SO_2; T. Sasaki, T. Itoh, J. Itoh and T. Ishikawa: The 13th ICC., Melbourne, Nov. 1996.

An Electrochemical and SERS Study of the Synergistic Effect of1-[(1',2'-Dicarboxy)ethyl]-benzotriazole and KI for the Inhibition of Copper Corrosion in Aerated Acid;V.Otieno-Alego,S.E.Bottle,T.Notoya & D.P.Schweinsberg:13th International Corrosion Congress, Melbourn, Australia, November, 1996.

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Our research activities are in characterization and evaluation of surface properties, surface reactions, surface compositions, and surface morphologies of materials.

The research programs in our laboratory are:

(1) Preparation and characterization of spinel type manganese oxide.

A spinel type manganese oxide ($\square Mn_2O_4$) with vacancies ($\square$) is a "lithium ion memory" template ion exchanger, and has shown promise for the recovery of lithium from sea water and preliminary concentration of trace lithium in natural environments. From a kinetic model analysis of the incorporation of Li into the oxide, it was found that there can be two incorporation processes: a faster surface reaction and a slower bulk reaction.

(2) Modeling and characterization of ion exchange properties of the surface of metal oxide particles as corrosion products, battery materials, and soil components.

The fine metal oxide particle/water systems are important in relation to many industrial and natural environmental processes. The acid-base, charge, and ion adsorption characteristics of metal oxides were evaluated by modeling, and it was shown that these characteristics can be explained with the electronegativity of oxides dfined by Sanderson. The Co (II) ion adsorption properties of metal oxides are also investigated.

(3) Dissolution of magnetite in chelating agent solutions.

The structural materials of cooling system of (nuclear) power plants are covered with metal oxides (magnetite and others) as corrosion products, and they cause inhibition of heat transmission and radioactive contamination due to incorporation of isotopes. The corrosion products are removed industrially by dissolution with chelating agents. The rate of dissolution of magnetite in EDTA solutions was modeled, and the effects of pH and oxyen were analyzed. It was found that the effect of pH is due to the pH dependencies of both the concentration of EDTA species and the transfer of lattice oxide ions by proton attack. In the presence of oxygen, the dissolution rate decreases, and this effect was suggested to be due to the loss of dissolved Fe(II)-EDTA chelate by oxygenation, as Fe(II)-EDTA can dissolve magnetite further without O_2.

(4) Initial stage of the high temperature oxidation of Fe-Cr and Fe-Ni-Cr alloys.

There are many works on the high temperature oxidation of Fe-Cr and Fe-Ni-Cr alloys. Many of them concerned with the long time oxidation and the number of the work on the initial oxidation is limited. Study on initial oxidation is important since it may give a information about the oxidation at much longer time and a useful information about operation of stainless steel production, especially descaling and annealing processes. In this work thin films grown on Fe-Cr alloys oxidized in 1 atm of oxidizing gas for 0 to 300 s at 1273 K were analyzed with several methods (TLXRD, XPS, AES-SAM, FTIR-RAS, and FE-SEM) sensitive to the surface properties. Effect of atmosphere, temperature, impurity metal on initial oxidation have been made to clear.

(5) Breakaway oxidation of Type 430 stainless steel

Breakaway oxidation is a type of abnormal oxidation frequently observed on Fe base alloys at high temperature especially in atmosphere containing water vapor. To explain the origin of the phenomenon and the effect of water vapor on it, XRD method was mainly employed and the following results were obtained. (a) Breakaway oxidation occurred when the film thickness attained a critical thickness which is different with atmosphere. (b) Breakage of the initially grown protective oxide film initiated before breakaway oxidation but broken part was cured itself. (c) Water vapor might affect the self-during action of protective oxide film and shorten the period of breakaway to occur.

(6) Thermal oxidation of Ti covered with metals and investigation of photoelectrochemical properties of the oxides.

TiO_2 are well known as its photosensitizing properties. As a result, it will be a candidate for solar cell, but larger bandgap energy make it unsuitable. In this study, composite oxides of Ti and M (M=W, Ta, Mo, Ni, Zn, and Cr) were prepared by thermal oxidation of Ti covered with metals as above and the photoelectrochemical response was measured. It was found that composite oxides containing W, Ta and Zn show higher anodic photocurrents than pure TiO_2

Other activities.

In June Dr. Tamura attended the 70th Colloid and Surface Science Symposium held at Clarkson University, Potsdam, N.Y., presenting a paper "The Co^{2+} Adsorption Abilities of Metal Oxides Evaluated with a Model Based on the Frumkin Isotherm".

Presentations

An XRD study of the oxide properties formed on Type 304 stainless steel at 1273 K; T. Saito, I. Saeki, H. Konno and R. Furuichi: The Hoint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn, Surf. Finish. Soc.. Jpn, and Jpn. Soc. Corros. Eng., Sapporo, Jan, 1996.

The photoelectrochemical properties of titanium oxide electrode containing transient metals prepared by thermal oxidation; N. Okushi, I. Saeki, H. Konno and R. Furuichi: The Hoint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn, Surf. Finish. Soc.. Jpn, and Jpn. Soc. Corros. Eng., Sappоro, Jan, 1996.

An improvement of the photoelectrochemical responce of TiO_2 by inclusion of transient metals; I. Saeki, N. Okushi, J. Setaka, R. Furuichi and H. Konno: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan, 1996.

Effect of the solution pH and the partial pressure of oxygen on the rate of incorporation of Li^+ into a spinel type manganese oxide -Evaluation by Modeling-; A. Tanaka, H. Tamura, and R. Furuichi: The 1996 Winter Joint Meeting

Joint Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1996.

Determination of the Kinetic Model Parameters for the Dissolution of Iron Oxides in the Removal of Radioacitive Contamination; H. Tamura, S. Takasaki, and R. Furuichi: The 70th Spring Annual Meeting of Chem. Soc. Jpn., Tokyo, Mar., 1996.

The photoelectoro responce of Ti-W or Ti-Zn oxides; N. Okushi, J. Setaka, I. Saeki, H. Konno and R. Furuichi: The 56 th Annual Meeting of Surf. Finish. Soc. Jpn., Chiba, Mar, 1996.

Change in the oxide properties of the oxide film due to breakaway oxidation; T. Saito, I. Saeki, H. Konno and R. Furuichi: The 42nd Annual Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1996.

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Modeling of Ion Adsorption for Pre-concentation of Analytical Samples; H. Tamura and R. Furuichi: The 1996 Summer Joint Meeting of the Hokkaido Secs. of Chem. Soc. Jpn. and Jpn. Soc. for Anal. Chem., Asahi kawa, Jul., 1996.

A Method to Evaluate the Acide-Base Properties of Lake and River Sediments; S. Kawamura, F. Terui, and H. Tamura: ibid.

Modeling of the Dissolution of an Analytical Sample; H. Tamura, S. Takasaki, and R. Furuichi: The 45th Annual Meeting of Jpn. Soc. for Anal. Chem., Sendai, Sept., 1996.

Acid-Base Properties of the Sediments of Nishiki-Onuma and Nishiki-Konuma in Tomakomai; S. Kwamura, F. Terui, and H. Tamura: The 61st Annual Meeting of Jpn. Limnol. Soc., Sapporo, Sept., 1996.

Modeling of Ion Exchange Properties of Metal Oxide Particle Surfaces -Evaluation of the Co(II) Ion Adsorption Properties of Metal Oxides-; H. Tamura: SRL Forum on Anti-corrosion Properties of Precipitate Type Films on Steel (Jpn. Steel Co.), Futtsu, Nov., 1996.

A Kinetic Model of the Chelateing Dissolution of a Metal Oxide; H. Tamura: The 5th Seminar of the Institute for Advanced Materials Processing, Tohoku University, Sendai, Nov., 1996.

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The current research activities of the laboratory are mainly concerned with corrosion of the metallic materials used in nuclear industry, development of fuel cells using reservoir alloys, estimation of pitting corrosion, migration of noble metal fission products in UO_2, thermal properties of cesium uranates, and radioactive waste management.

Current research topics include:

(1) The corrosion behavior of the candidate overpack materials in bentonite is being studied for safety assessment of the geological disposal of the high level radioactive waste. At present, average corrosion rates of iron and apparent diffusion coefficients of corrosion products have been determined, using neutron-activated iron foils and bentonite specimens with

different dry densities. The corrosion rates and diffusion coefficients depend upon the dry density of the bentonite. Quantitative analysis of the corrosion products was also carried out using 1,10-phenanthroline as a colorimetric indicator to obtain the concentration profiles of both Fe^{2+} and total Fe concentrations and of the Fe^{2+}–total Fe ratio. From the profiles, it is probable that the pH and/or redox potential of the pore water in bentonite can be changed by corrosion of iron.

(2) Migration of radionuclides in compacted bentonite, which is the most promising candidate for buffer material in geological disposal of the HLW, is considered to be dominated by diffusion because of its low permeability of water. In addition, significant retardation effects, caused by the high absorbing ability of bentonite, can be also expected when the radionuclides are cations. Therefore, the diffusion and sorption behavior are very important studies for performance assessment of the geological disposal, and have been extensively investigated. A pore water diffusion model, in which radionuclides are supposed to diffuse through free water in the pores of clay even at high clay dry density, has been generally adopted to explain the diffusion behavior. It is, however, pointed out that apparent diffusion coefficients were underestimated by the diffusion model at higher clay density. Also, surface diffusion, in which cations sorbed on clay migrate on the clay surfaces, has been proposed as an additional diffusion process. We have been studying the diffusion mechanism of radionuclides over a wide range of clay densities, by determination of the activation energies for the apparent diffusion coefficients of Na^+, Cs^+, Sr^{2+} and Cl^- ions in the compacted clays and by the XRD measurements of basal spacings of the compacted clays. Thus far we have found evidence for changes in diffusion processes as a function of clay density. Pore water diffusion, surface diffusion and interlayer diffusion appear to be dominant diffusion process at low, intermediate and high clay densities, respectively.

(3) In connection with the long-term prediction of the migration behavior of radioactive nuclides in compacted bentonite, the vapor pressure of the

water in bentonite (Kunigel-V1) has been measured as a function of water content and temperature, under an external pressure free condition. Relative partial molar Gibbs free energy $\Delta G(H_2O)$, enthalpy $\Delta H(H_2O)$ and entropy $\Delta S(H_2O)$ of the water were determined at temperature of 298.15K. The interlayer distance of montmorillonite in bentonite was found to be three water layers at a water content of 20.3 wt% as measured by the X-ray diffraction method. One third of the water in bentonite at the water content is similar to ordinary water, but is not regarded as a dilute electrolytic solution. One fourth of the total water of the bentonite at the water content is bound water; the relative partial molar entropy of the water is from the full to a half of the entropy of solidification of water. The thermodynamic quantities are considered to be a function of the water content in the forms of pore water, interlayer water in montmorillonite and adsorbed water on other minerals. In addition, to clarify the kinetic properties of water in bentonite, the diffusion of tritiated water in compacted bentonite has been studied as a function of temperature and dry density using liquid scintillation counting .

(4) Hydrogen gas is expected after the disposal of HLW to be generated from corrosion of the overpack which is made of carbon steel. This could result in an increase of gas pressure at the inside of the buffer materials surrounding the overpack, since the buffer has high sealing ability. In order to ensure the long-term integrity of the repository, it is necessary to estimate the hydrogen evolution rate and to understand the migration behavior of the gas in the buffer materials. In this study, the diffusion coefficient of helium gas in compacted montmorillonite was studied instead of hydrogen gas. Diffusion experiments for helium was carried out for water-saturated, compacted montmorillonite pellet at the dry density of 1.0 Mg m^{-3} in distilled water, in which helium was saturated by bubbling. After a prescribed time, the montmorillonite pellet was sliced, and helium gas content in each slice was measured with QMS. The apparent diffusion coefficient of 0.9×10^{-11} m^2s^{-1} was obtained from the helium concentration profile. In addition, the amount of helium was found to be 0.5×10^{-6}g

/g- water-saturated montmorillonite. This indicated that helium gas migrated in the compacted montmorillonite as dissolved gas, and that the migration was not affected by the sorption of the gas on the clay mineral.

(5) For safety assessment of land disposal of radioactive waste, the migration behavior of fission products and actinides in geologic formation must be clarified. In this connection, the stability constant of Sr^{2+} with humic acid was determined using ^{85}Sr as a radiotracer. Sorption coefficients of Sr^{2+} on kaolinite were measured by a batch method as a function of contact time, pH, and the concentrations of Sr^{2+} and humic acid (HA). The K_d values increased with pH under the conditions both with and without HA. The K_d values in the presence of HA remained virtually unchanged with increasing HA concentration up to several tens of ppm, in comparison with the values in the absence of HA. On the other hand, at higher HA concentrations, the K_d values decreased with increasing HA concentration at pH above 5. A model was proposed, in which the effect of HA on K_d of Sr (II) ions onto kaolinite was described in terms of the sorption coefficient of Sr(II) ions in the absence of HA , K_d^0; the sorption ratio of HA on kaolinite, f_{HA}; and the stability constant of Sr(II) humate, β . These parameters were treated as input data in the model calculation to obtain K_d as a function of pH and HA concentration. Despite the simple mathematical model, the K_d values estimated by the model calculation were in good agreement with the experimental data.

(6) Pd is the most SiC-corrosive noble metal fission product in coated particle fuels for high temperature gas-cooled reactors. To clarify the effects of Pd on the fuel performance, the migration behavior of Pd in uranium dioxide pellets has been studied. Penetration profiles of Pd in the pellets were obtained by electron probe microanalysis. Diffusion coefficients of Pd in UO_2 were determined at temperatures from 1600 to 2100K. The diffusion coefficients were in the order of 10^{-15} m^2s^{-1}, though the vapor pressure of Pd is 10^{-3} torr at 1700K. A model of the gaseous diffusion of Pd through pores in UO_2 retarded by the formation of U-Pd alloy was

proposed.

(7) Thermal expansion and thermal conductivity of cesium molybdate have been investigated. The temperature dependence of the lattice parameters of Cs_2MoO_4 was measured using high-temperature X-ray diffraction from ambient temperature to 773 K. The linear thermal expansion of Cs_2MoO_4 obtained from the temperature dependence of the lattice parameters was about 2% at 773 K, which was more than four times that of UO_2. The thermal diffusivity in Cs_2MoO_4 was measured by the laser flash diffusivity method from room temperature to 1000 K. Further, the thermal conductivity of Cs_2MoO_4 was evaluated from the measured thermal diffusivity, bulk density, and the literature value of the specific heat capacity. The thermal conductivity of Cs_2MoO_4 increased with temperature above 400 K, and was about 5% of that of UO_2 at 300 K and less than 20% at 1000 K. Further, the thermal properties of cesium uranates, Cs_2UO_4 and $Cs_2U_2O_7$, and their effects on the UO_2 fuel performances were investigated. The conditions of formation of the cesium uranates were estimated by the CHEMSAGE code. The cesium uranates were prepared from U_3O_8 and Cs_2CO_3, and identified by X-ray diffraction. The temperature dependence of the thermal expansion coefficients of Cs_2UO_4 and the thermal conductivities of $Cs_2U_2O_7$ were determined. It was found that there is an anisotropy between the thermal expansion coefficients in a- and c- axes, and their geometric mean was much larger than the thermal expansion coefficient of UO_2. The thermal conductivity of $Cs_2U_2O_7$ was smaller than that of UO_2, and it is anticipated that the temperature of the UO_2 fuel appreciably rises when $Cs_2U_2O_7$ forms in the periphery of UO_2 pellets.

(8) Relationships between kinetics of hydrogen absorption and hydrogen concentration profiles of Ti and Zr by electrolysis were investigated by nuclear, chemical and other conventional techniques. Hydrogen atoms interact very intensively with each other in the metal. Hydrogen concentration profiles were dependent on the condition of cathodic electrolysis and pre-treatment of metals. A high level of hydrogen concentration in the

surface layer was realized by electrolysis at high cathodic current density for a prolonged time. The rate of hydrogen absorption was influenced strongly by the formation of a layer having high hydrogen concentration.

(9) Processes of passivation and localized corrosion of metals were studied with a laser displacement equipment. The changes of displacement and reflection were simultaneously and continuously recorded with the change of corrosion current as the digital data. These data are divided into direct-current and alternating-current components. The alternating-current component can be calculated and changed into a frequency spectrum by maximum entropy method. The spectrum shape was expressed as the slope and magnitude. The shapes of the spectra during the corrosion were expressed by the relationship

$I=F^n$,

where $(-1 < n < 0)$, in the range of frequency from 10^{-2} to 10 Hz. The method was applied for estimation of the stability of passive films in a solution, connecting with a relationship between film displacement and corrosion current. The method can apply to predict the possibility of pit generation.

Other activities

Assoc. Prof. Dr. S. Sato attended the 14th IUPAC Conference on Chemical Thermodynamics in August, Osaka, Japan and presented the paper entitled "Migration Behavior of Pd in UO_2".

He attended International Workshop on Interfacial Effects in Quantum Engineering system (IEQES-96) held in Mito, Japan in August, and presented the paper entitled "Effect of Humic Acid on the Sorption of Neptunium onto Kaolinite".

Res. Assoc. Dr. T. Mizuno attended the Second International Conference of a low Energy Nuclear Reaction at Texas A & M University, USA in September to present a paper entitled "Anomalous Element Depositions and Isotopic Changes on Palladium Cathode after Cathodic Electrolysis".

Res. Assoc. Mr. T. Kozaki attended the 1996 Material Research Society Fall Meeting on the Scientific Basis for Nuclear Waste Management XX, Boston, USA in December to present a paper entitled "Effect of dry density on activation energy for diffusion of strontium in compacted sodium montmorillonite".

Foreign researchers visited the NUCLEAR MATERIAL SYSTEM LABORATORY in October include Professor Richard A. Oriani from the University of Minnesota, and Professor O. J. Kleppa of the University of Chicago.

Presentations

Study on corrosion behavior of iron in bentonite using activated iron foil; Tamotsu Kozaki, Yuji Imamura, Hideaki Tamai, Hideki Kawabe, Seichi Sato, Hiroshi Ohashi, Jitsuya Takada and Hirotake Moriyama, the Scientific Meeting of the Research Reactor Institute, Kyoto University, Kumatori-cho, January, 1996.

Diffusion of cesium ions in compacted Na-montmorillonite; Atsushi Fujishima, Hiroki Sato, Tamotsu Kozaki, Seichi Sato and Hiroshi Ohashi, The 1996 Annual Meeting of The Atomic Energy Society of Japan, Osaka, March, 1996.

Diffusion of cations in compacted Na-montmorillonite; Tamotsu Kozaki, Atsushi Fujishima, Hiroki Sato, Seichi Sato and Hiroshi Ohashi, The 31th Annual Meeting of The Japan Health Physics Society, Sapporo, May, 1996.

Activation energy for diffusion of strontium ions in compacted Na-montmorillonite, Tamotsu Kozaki, Hiroki Sato, Atsushi Fujishima, Nobuhiko Saito, Seichi Sato and Hiroshi Ohashi, The 1996 Fall Meeting of The Atomic Energy Society of Japan, Sendai, March, 1996.

Anomalous Element Depositions and Isotopic Changes on Palladium Cathode after Cathodic Electrolysis; Tadahiko Mizuno, Tadayoshi Ohmori, Tadashi Akimoto, Kazuhisa Azumi, Masatoshi Kitaichi, Kohichi Inoda, Kazuya Kurokawa and Michio Enyo, Second International Conference of a low Energy Nuclear Reaction, Texas A & M University, USA, September 13-14 (1996).

Temperature Dependency on Counting Efficiency of NE213 Liquid Scintillatorlator for Low Level Neutron Measurement; Tadashi Akimoto, Tadahiko Mizuno, Takashi Saito, Ikuo Murai and Toshiaki Kumada, Sixth International Conference on Cold Fusion, Hotel Apex, Toya, Hokkaido, Japan, October 13-18 (1996).

Isotopic Distribution for the Elements Evolved in Palladium Cathode after Electrolysis in D_2O Solution; Tadahiko Mizuno, Tadayoshi Ohmori, Tadashi Akomoto, Kazuya Kurokawa, Masatoshi Kitaichi, Kohichi Inoda, Kazuhisa Azumi, Sigezo Shimokawa and Michio Enyo. Sixth International Conference on Cold Fusion, Hotel Apex Toya, Hokkaido, Japan, October 13-18 (1996).

Production of Heavy Metal Elements and the Anomalous Surface Structure of the Electrode Produced during the Light Water Electrolysis on Au Electrode; Tadahiko Mizuno, Tadayosi Ohmori and Michio Enyo, Sixth International Conference on Cold Fusion, Hotel Apex, Toya, Hokkaido, Japan, October 13-18 (1996).

Effect of dry density on activation energy for diffusion of strontium in compacted sodium montmorillonite; Tamotsu Kozaki, Hiroki Sato, Atsushi Fujishima, Nobuhiko Saito, Seichi Sato and Hiroshi Ohashi, 1996 Material Research Society Fall Meeting on Scientific Basis for Nuclear Waste Management XX, Boston, USA, Dec. 2-6, 1996.

INTERFACIAL ELECTROCHEMISTRY LABORATORY

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The research activity of the laboratory still continues to be directed towards a better understanding of the interfacial properties of metal and semiconductor electrodes in relation to the interfacial electrochemistry involving adsorption, corrosion, passivation, anodic oxidation, and surface finishing.

Current topics on research are as follows :

(1) Piezoelectric Detection of Changes in Surface Energy of Iron Electrode

The piezoelectric technique which is capable of detecting small changes in surface energy of solid electrode, is applied to iron electrode in order to investigate adsorption of electrolyte anions on iron. The potential of zero charge (pzc) of iron electrode could be evaluated from the piezoelectric signal curves. It is found from pzc of iron that the strength of contact adsorption of electrolyte anions on iron is in the order of $Cl^- = Br^- = I^- > SO_4^{2-} > ClO_4^-$.

The piezoelectric signals of iron electrode covered with passive film are measured in deaerated pH 8.4 borate solutions with and without SO_4^{2-} ions. The electrostriction as well as surface tension of passive film would contribute to the piezoelectric signals to some extent. The amplitude, $|A|$, of piezoelectric signals in the passive potential region increased with increasing concentration of SO_4^{2-} ions, suggesting that adsorption of SO_4^{2-} ions on passive film increases the surface charge density of passive film or the potential drop across the passive film / solution interface, which would influence the stability of passive film.

(2) Corrosion Kinetics of Iron Thin Film in Deaerated Phosphate Solutions by an EQCM

The corrosion rates of iron thin film in deaerated phosphate solutions were measured by an EQCM as a function of solution pH or phosphorus concentration in solutions. The dependences of corrosion rate and corrosion potential on solution pH and phosphorous concentration have suggested that the corrosion mechanism changes in the vicinity of pH 5 and $H_2PO_4^-$ contributes to both anodic dissolution of iron and hydrogen evolution. The corrosion mechanism in which iron-phosphate-hydroxide complex ion as an adsorbed intermediate was taken into consideration was proposed to explain the experimental results.

(3) Measurement of Membrane Potential of PbO_2 and $PbSO_4$ Prepared on Platinum Net Electrode with Electrosynthesis.

β-PbO_2 was anodically deposited on platinum net electrode in $PbNO_3$ aqueous solution. The ion-selective permeability of β-PbO_2 was evaluated from the measurement of membrane potential, which showed that β-PbO_2 is cation selective for KCl, NaCl, KNO_3, and Na_2SO_4 aqueous solutions.

Moreover, β-PbO_2 was electrochemically converted to $PbSO_4$ in 1M H_2SO_4. The measurement of membrane potential showed that $PbSO_4$ thus converted is anion selective for KCl, NaCl, KNO_3, and Na_2SO_4 aqueous solutions. The reversible changes in ion-selective permeabilty were observed during electrochemical conversion between β-PbO_2 and $PbSO_4$ in 1 M H_2SO_4.

(4) Stability of Titanium Oxide Film in Deaerated Neutral Solutions

Stability of the anodic oxide film formed on titanium under the deaerated aqueous environment was examined using impedance monitoring technique. The oxide film looses its electric resistivity with a polarization period at the potentials around the immersion potential for 32 h. This change was connected to the hydrogen atom penetration into the oxide film

(5) Electrochemical Analysis of the Double Zincate Process of Aluminum Alloys

Zinc deposition on Al and Al-Mg alloys were examined using SEM observation, EPMA, and potential trace. Shape of Zn deposition is affected by the concentration of zincate solution, additive such as Fe^{3+}, and composition of the substrate. For example, higher concentrations of NaOH and ZnO leads rapid dissolution of the Al oxide layer and Al substrate, and thus faster Zn deposition. Existence of Fe^{3+} ions results in the growth of rather small, non-hexagonal Zn particles due to co-deposition of Fe onto Zn deposition. In the second zincate process, a stratiform Zn layer grows to cover the Al substrate in a zincate solution without Fe^{3+} ions. It also provides granular Zn deposition in the 2nd zincate treatment because the co-deposition of Fe may suppress the Zn deposition in the lateral dimension. Such granular Zn deposition provides a sufficient anchor effect for subsequent electroless Ni plating.

(6) Construction of Scanning Electrochemical Microscope for Evaluation of Heterogeneity of Passive Film and Its Application to Iron Electrode

A scanning electrochemical microscope (SECM) was constructed to evaluate the heterogeneity of passive films on metals and applied to iron electrode passivated in deaerated pH 8.4 borate solution. The probe current image and specimen current image for the specimen electrode, which consists of two iron plates embedded into epoxy resin, were measured with a tip-generation/substrate-collection (TG/SC) mode in deaerated pH 8.4 borate solution containing $[Fe(CN)_6]^{4-}$ as a mediator. The probe current image as compared with the specimen current image could distinguish between epoxy resin and each iron plate, and also evaluate the difference in thickness of passive film between two iron plates. The lateral resolution of the probe current image was about 40 μ m which was two times as much as the diameter (20 μ m) of the probe electrode.

(7) Changes in Luminescence Properties of Porous Silicon Layer due to Anodic Oxidation

A porous silicon layer (PSL) was prepared on p-type single crystal Si (100) wafer with an electrochemical etching in ethanol solution of 22.6 wt% HF solution. A galvanostatic oxidation of PSL until 500 V (SHE) in 0.1 M KNO_3 ethylene glycol solution was performed to improve visible photoluminescence (PL) properties of PSL. Moreover, an electroluminescence (EL) emitted from PSL during anodic oxidation was measured to understand anodic oxidation mechanism of PSL. The TEM image and FTIR spectra have indicated that PSL as prepared consists of Si nanoparticles with a diameter of 2 nm - 3 nm, and the Si nanoparticles are covered with silicon hydrides, SiH_X.

At the initial stage of anodic oxidation of PSL where the potential remains a low value, silicon hydrides on Si nanoparticles are firstly oxidized to elemental Si and simultaneously an EL with a peak wavelength of 800 - 710 nm is emitted from the PSL. In the subsequent oxidation region where the potential rises linearly with time, Si nanoparticles are oxidized to SiO_2 and simultaneously an EL with two peak wavelength of 650 and 520 nm is emitted from the PSL. The origins of these EL emission sources were explained by using an electronic band model of the Si /SiH_X / solution interfaces or Si /SiO_2 /solution interfaces.

The PL spectra of PSL as prepared have a peak wavelength of 660 nm. The PL intensity increases and the PL spectra shifts as anodic oxidation of PSL proceeds. It has been discussed by using the electronic band model that the decrease in surface state density of Si nanoparticles due to anodic oxidation would enhance significantly the PL intensity. The above results support that the quantum confinement effect is operative in the visible PL of PSL subjected to anodic oxidation.

Other Activities

In July, Prof. M. Seo was invited to Gordon Research Conference on Aqueous Corrosion in New Hampshire and presented the paper entitled " Corrosion of Fe, Formation and Interfacial Properties of Oxide Films on Fe". Prof. M. Seo and Mr. K. Shigyo (Ph.D. Student) attended the 47th Annual Meeting of the International Society of Electrochemistry which was held in Veszprem-Balatonfured, Hungary on September and presented two papers entitled "Piezoelectric Detection of Changes in Surface Energy of Au Electrode due to I- and Br- Adsorption" and "Electrochemical Control of Luminescence Properties of Porous Silicon". Afterward, Prof. M. Seo visited Prof. D. Landolt at Laboratoire de Metallurgie Chimique, Ecole Polytechnique Federale, Lausanne, Swizerland and presented the Seminar on In-Situ Gravimetry of Corrosion of Iron Thin Films.

The following foreign scientists visited this laboratory : Dr. M. Gattrell ,Institute for Chemical Process and Environmental Research Technology, National Research Council of Canada on February 29 - March 3, Prof. R. Oltra, Laboratoire de Recherches sur la Reactivite des Solides, Universite de Bourgogne, France on April 16 - 18, Prof. R. A. Oriani, Department of Chemical Engineering and Materials Science, University of Minnesota, USA on October 9 -11, Ms. K. Marisa, National Center of Catalysis, National University of Litoral, Argentina, Dr. T. Hassan, Chemistry Department, Faculty of Science, Al-Azhar University, Egypt, Mr. B. A. Mohamed, Chemistry Department, Faculty of Science, Helwan University, Egypt, Dr. J. L. R. Cerda, School of Chemical Engineering, Michoacan University, Mexico, Ms. F. I. Abarquez, Fuels and Energy Division, Industrial Technology Development Institute, Philippines, Ms. E. B. Quinay, Pablo Borbon Memorial Institute of Technology, Philippines on October 22, Prof. R. Winand, Materials Science and Engineering Department, Faculty of Applied Sciences, Universite Libre de Bruxelles, Belgium on December 10.

Presentations

Study on Au/I-, Br- Interfaces by a Piezoelectric Detection ; K. Ueno and M. Seo : The 1996 Joint Meeting of Hokkaido Sec. of Electrochem. Soc. Jpn, Surf. Finish. Soc. Jpn, and Jpn. Corros. Eng., Sapporo, Jan., 1996

Influence of Electrochemical Etching Current Density on Luminescence Properties and Microstructure of Porous Si ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi : ibid.

Trace of Property Change of the Passive Film on Titanium ; G. Yamamoto, K. Azumi and M. Seo : ibid.

Trace of the Double Zincate Process of Aluminum ; Y. Fujishige, K. Azumi, M. Seo, H. Nakao and K. Tashiro : ibid.

Changes in Surface Morphology of Carbon Steel Subjected to Corrosion in Deaerated Carbonate Solution ; K. Suzuki, K. Fushimi, K. Azumi and M. Seo : ibid.

An EQCM Measurement of Corrosion Rate of Electroplated Iron Thin Film in Phosphate Solution ; M. Kurosaki and M. Seo : ibid.

Electrochemical Control of Luminescence Properties and Microstructure of Porous Silicon ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi : The 93rd Annual Meeting of Surf. Finishing Soc. Jpn., Chiba, March, 1996

Electrochemical Study of the Double Zincate Process of Alminum Alloy ; K. Azumi, Y. Fujishige, M. Seo, H. Nakao and K. Tashiro :ibid.

Possibility of Evaluating Heterogeneity of Passive Film with Semiconductor Electrode Characteristics ; M. Seo, K. Fushimi and W. H. Smyrl : Special Seminar on Application of Semiconductor Electrode to Corrosion Engineering, Jpn. Soc. Corros. Eng., Tokyo, May,1996

Pursuit of Electronic Property Change of the Passive Film on Titanium ; K. Azumi, G. Yamamoto and M. Seo : The 1996 Annual Meeting of Jpn. Soc. Corros. Eng., Tokyo, May, 1996

Pursuit of Corrosion Behavior of Electroplated Iron Thin Film in Deaerated Phosphate Solution ; M. Seo, M. Kurosaki and M. D. Ward : ibid.

Observation of Changes in Surface Morphology of Corroded Carbon Steel ; M. Seo, K. Suzuki, K. Fushimi, K. Azumi and W. H. Smyrl : ibid.

Corrosion of Fe, Formation and Interfacial Properties of Oxide Films on Fe ; M. Seo : Gordon Research Conference on Aqueous Corrosion, New London, New Hampshire, USA, July,1996

Piezoelectric Detection of Changes in Surface Energy of Au Electrode due to I- and Br- Adsorption ; M. Seo and K. Ueno : The 47th Annual Meeting of the Inernational Society of Electrochemistry, Veszprem - Balatonfured, Hungary, Sept.,1996

Electrochemical Control of Luminescence Properties of Porous Silicon ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi : ibid.

Evaluation of Electrode Interface by a Piezoelectric Detection of Change in Surface Energy ; M. Seo : The Fall Meeting of Electrochem. Soc. Jpn., Kusatu, Japan, Sept.,1996

Construction of Scanning Electrochemical Microscope and Its Application to Passive Films on Iron ; K. Fushimi and M. Seo : The 119th Annual Meeting of Jpn. Inst. Metals, Sapporo, Sept., 1996

Influence of Surface Composition of Si Nanoparticles on Luminescence Properties of Porous Si ; K. Shigyo, M. Seo, K. Azumi and H. Takahashi: ibid

An EQCM Measurement of Corrosion Behavior of Electroplated Iron Thin Film in Deaerated Phosphate Solution - pH Dependence of Corrosion Rate ; M. Kurosaki and M. Seo :ibid.

Piezoelectric Detection of Changes in Interfacial Energy of Iron / Aqueous Solution ; K. Ueno and M. Seo : ibid.

Changes in Surface Morphology of Carbon Steel and Pure Iron Subjected to Corrosion in Deaerated Carbonate Solution ; K. Suzuki, K. Fushimi, K. Azumi and M. Seo : ibid.

Property of Thin Oxide Films on Metals ; K. Azumi and M. Seo : 5th Joint Seminar between Hokkaido Univ. and Univ. Science and Tech. Beijing ,Hokkaido University, Sept., 1996

Tentative Evaluation of Passive Film on Iron by a Scanning Electrochemical Microscope ; K. Fushimi, M. Seo and E. Fujimoto : The 43rd Discussion Meeting of Jpn. Soc. Corros. Eng., Osaka, Oct., 1996

Measurement of Potential of Zero Charge for Iron Electrode by a Piezoelectric Response Method ; M. Seo and K. Ueno : ibid.

Distribution of Charge and Potential at the Metal / Solution Interface ; M. Seo and K. Ueno : Research Meeting on New Materials and New Technology for Environment and Energy, Institute for Materials Research, Tohoku University, Sendai, Nov., 1996

DISSIMILAR MATERIALS INTERFACE ENGINEERING LABORATORY

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Mr.Ishida returned to Kobe Steel in February after his stay in Sapporo for 10 months. Assoc. Prof. Yu Jinming joined as a visiting researcher from Institute of Corrosion and Protection of Metals Academia Sinica, China in July.

The research activity of the laboratory is directed to an understanding of the mechanism of high temperature corrosion of materials, and developing the corrosion resistant alloys and corrosion protection technique at high temperature. The research activity is also directed to an understanding of the solidification mechanism of metals and Alloys.

Current topics on research are in the following:

(1) High temperature sulfidation of alloys

Sulfidation properties of stainless steels, nickel alloys, and Ti-Al intermetallic compounds were investigated at relatively low sulfur pressures in H_2S-H_2 atmospheres.

(2) High temperature nitriding of alloys

Nitridation properties of Ti-Al intermetallic compounds were investigated in nitrogen atmospheres with or without impurity oxygen.

(3) Ceramic-Metal joining

Silicon nitride ceramics were joined to metals using active alloy solders such as Ni-Cu-Ti and Ag-Cu-Ti, and the new bonding process was developed. Zirconia-metal joining was investigated for development of SOFC.

(4) TLP Bonding

Dissolution and isothermal solidification behavior during transition liquid phase bonding process of Ni and Ni base alloys were investigated based on both experiment and computer simulation.

(5) Ultrasonic micro-spectroscopy

Scanning acoustic microscope was used to determine the residual stress by making use of the principle concept basing on the measurement of SAW velocity and its change in stress. This novel method was successfully applied to the ceramic-metal joints, ion-exchanged glasses, and Ag-ion diffused layer in glasses.

(6) Galvanizing process of steels by hot Zn-Al and Al-Si dippings

Galvanizing of steels was carried out by using Zn-Al and Al-Si molten alloys, and the optimum condition was investigated to make a galvanized layer having high corrosion resistance.

(7) Characterization of thermal barrier coatings

Thermal barrier coatings of the NiCrAlY-Zirconia composite were prepared by using Plasma Splay Coating Method and their mechanical and physical properties were investigated.

(8) Pb-free solder

In order to design Pb free solder, change in microstructure and mechanical properties of Sn-Bi alloys during thermal cycle were investigated.

(9) Corrosion resistant aluminum cast iron.

In order to develop a low cost and corrosion resistant material, cast iron containing high content of aluminum was made, and its properties were evaluated.

(10) Molecular dynamics simulation of grain boundary formation

The Structure and the properties of the grain boundary of iron were investigated by Molecular Dynamics Simulation. Change in properties such as grain boundary energy and grain boundary strength in relation to the crystal orientation difference were estimated.

(11) Computer simulation of grain structure formation of casting

A new method to simulate the grain structure formation in casting was investigated by combining Monte-Calro Method and heat transfer analysis.

Other activities

Prof. Narita attended the 4th International Symposium on High Temperature Corrosion and Protection of Materials held at Les Embiez, France, in May, and presented the paper entitled " The Nonstoichiometry and Chemical Diffusivity of Iron-Chromium Sulfide $(Fe,Cr)_{1}$-$_{\delta}S$ ". Prof. Narita attended the 4th International Conference on ADVANCES SURFACE ENGINEERING, at Newcastle Upon Tyne, UK, in May ,and presented the paper entitled "High Temperature Sulfidation of Ti-Al Intermetallic Compound and Improvement in Their Anti-Oxidation Properties". Prof. Narita and Mr Hata attended the 8th JIM International Symposium on Interface Science and Materials Inter-connection held at Toyama in Jun, and presented the paper entitled "The Effect of Ceramic Strength on the Fracture Strength of Si_3N_4 Ceramic-Metal Joints". Mr. K.A.Z.Thosin attended the Scientific Meeting of Indonesian Student for Science and Technology in Japan held at Tokyo in April, and the paper entitled "Imaging of Surface Structure of Ag Ion Diffused Glasses by a Scanning Acoustic Microscope" was presented. In June, Prof. Narita and Mr. K.A.Z.Toshin attended the meeting of Indonesian Institute of Science at Bandung and presented the papers entitled "Scanning Acoustic Microscopy and its Application on Material Characterization" and "Measurement of Surface Elasticity of Ag Ion Diffused Glases using SAM.". In December, Prof. Narita attended the 13th International Corrosion Congress at Melbourne,Australia, and presented the paper entitled " Diffusional Analysis of Fe-Cr Alloy Sulfidation With Surface and Intergranular Sulfide Growth ".

Assoc. Prof. Ohsasa stayed at Massachusetts Institute of technology, U.S.A as an overseas researcher of the Ministry of Education of Japan for six months from April to September..

Foreign researchers visited the DMIE laboratory are Prof. Weitao Wu, Institute of Corrosion and Protection of Metals Academia Sinica, China in September, Prof. D.J.Young and Assoc. Prof. O.Ostrovski, The University of New South Wales, Australia in December.

Presentations

Diffusional Analysis of Fe-Cr Alloy Sulfidation With Surface and Intergranular Sulfide Growth; T.Narita, M.Noguchi, S. Kawamori and T. Yamamoto: 13th International Corrosion Congress.,Melbourne, Australia,Nov. ,1996.

The Nonstoichiometry and Chemical Diffusivity of Iron-Chromium Sulfide $(Fe,Cr)_{1-\delta}S$; T.Narita, M.Noguchi and T.Yamamoto: 4th International Symposium on High Temperature Corrosion and Protection of Materials, Les Embiez, France,May,1996.

High Temperature Sulfidation of Ti-Al Intermetallic Compounds and Improvement in Their Anti-Oxidation Properties; Narita and T.Yoshioka: 4th International Conference on ADVANCES SURFACE ENGINEERING, Newcastle upon Tyne, UK,May,1996.

The Effect of Ceramic Strength on The Fracture Strength of Si_3N_4 Ceramic-Metal Joints; S.Hata and T.Narita: 8th JIM International Symposium on Interface Science and Materials Inter-connection, Toyama, June , 1996.

Imaging of Surface Structure of Ag Ion Diffused Glasses by a Scanning Acoustic Microscope; K.A.Z.Thosin, T.Narita and I.Ishikawa: Scientific Meeting of Indonesian Student for Science and Technology in Japan, Tokyo,April,1996.

Scanning Acoustic Microscopy and its Application on Material Characterization; T.Narita: Indonesian Institute of Science, Bandung, June ,1996.

Measurement of Surface Elasticity of Ag Ion Diffused Glases using SAM; K.A.Z.Toshin, T.Narita and I.Ishikawa: Indonesian Institute of Science, Bandung, June ,1996.

Reactivity Between Si_3N_4 Ceramics and Ni-Cu-Ti Solder (I); S.Hata and T.Narita: The 118th Annual Meeting of Jpn. Inst. Metals., Tokyo, April. ,1996.

Thermal Cycle Behavior of 42Inver-Sn Joint; Y.Mizuno, S.Hata and T.Narita: The 118th Annual Meeting of Jpn. Inst. Metals., Tokyo, April. ,1996.

Non-stoichiometry of Iron-Chromium Sulfide $Cr_{1-\delta}S$; T.Yamamoto, M.Noguchi and T.Narita: The 118th Annual Meeting of Jpn. Inst. Metals., Tokyo, April. ,1996.

Prediction for Life of Oxidation Resistance of Pre-Sulfidation Treated TiAl; The 118th Annual Meeting of Jpn. Inst. Metals., Tokyo, April. ,1996.

High Temperature Oxidation Behavior of Nitrided TiAl Alloy; T.Yoshioka, T.Watanabe and T.Narita: The 119th Annual Meeting of Jpn. Inst. Metals., Sapporo, Sept. ,1996.

High Temperature Oxidation of Al Plated Fe-18Cr Alloy; T.Azuma, J.Tanaka and T.Narita: The 119th Annual Meeting of Jpn. Inst. Metals., Sapporo, Sept. ,1996.

Scale on Plasma Splayed MCrAlY Alloy Formed by High Temperature Oxidation; H.Taumi, M.Nakamori, Y.Harada and T.Narita: The 119th Annual Meeting of Jpn. Inst. Metals., Sapporo, Sept. ,1996

Non-stoichiometry and Inter-Diffusion Coefficients in Iron-Chromium Sulfide $(Fe,Cr)_{1-\delta}S$; T.Yamamoto, M.Noguchi and T.Narita: The 119th Annual Meeting of Jpn. Inst. Metals., Sapporo,Sept. ,1996.

Non-stoichiometry and Inter-Diffusion Coefficients in Iron-Chromium Sulfide $(Fe,Cr)_{1-\delta}S$; T.Narita, M.Noguchi and T.Yamamoto, M.Noguchi and T.Narita: The 119th Annual Meeting of Jpn. Inst. Metals., Sapporo,Sept. ,1996.

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INTERFACE MICRO-STRUCTURE ANALYSIS LABORATORY

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Mrs. Song-Zhu Chu, Northeastern Univ. in Shenyang, China, joined as a research student in November.

The research activity of the laboratory is still directed to an understanding of structure and properties of anodic oxide films on aluminum and its alloys, and the corrosion resistant materials at high temperatures. Surface patterning of aluminum is also attempted by laser irradiation and metal deposition for developing a new technology of micro components.

Current topics on research are in the following:

(1) In situ AFM observation of the surface of aluminum during anodizing.

The change in the surface morphology of aluminum during anodizing was observed by in situ AFM measurements, and compared with that by transmission electron microscopy. The surface roughness decreased with increasing anode potential, and this was explained in terms of the current distribution and Pilling- Bedworth ratio during film growth.

(2)Localized Ni deposition on aluminum with YAG-laser irradiation.

Aluminum specimens covered with porous anodic oxide films with different thicknesses were irradiated with pulsed YAG-laser to examine how the oxide film is removed by laser irradiation. Clacks were formed in all oxide films at the periphery of laser irradiated area, and this was more remarkable for thicker oxide films. Oxide films dyed with alizarin-red S showed a removal without any clacks, and this may be due to laser-energy absorpition by the oxide film. After laser irradiation, the specimen was cathodically polarized under potentiostatic conditions. Nickel layer was found to deposit at laser irradiated area effectively.

(3) Formation and breakdown of anodic oxide films in dilute KOH solutions

Aluminum was anodized galvanostatically in KOH solutions at $5x10^{-3}$, $5x10^{-4}$, $5x10^{-5}$ M at 293 K. At $5x10^{-5}$ M, anode potential, E_a, increased at a constant rate up to 400 V, and between 400 and 600 V, E_a increases at a slow rate. The rate of increase in E_a between 600 V and 1600 V was as high as that at the initial stage, and above 1600 V, the rate of increase in E_a decreased with E_a. The time variation in E_a at $5x10^{-4}$ M was similar to that at $5x10^{-5}$ M, except that the final stage started at 1200 V. At $5x10^{-3}$ M, E_a remained zero for initial 1500 s of anodizing, and then increased linearly with time, reaching a steady value of 600 V.

(4) Anodizing of aluminum covered with TiO_2 films formed by CVD.

Aluminum was initially covered with TiO_2 film by a chemical vapor deposition technique with tetra-iso-propyl titanate. The TiO_2 covered specimens were anodized galvanostatically in a neutral boric acid / borate solution. As anode potential increased, oxide films grew, which were composed of an outer TiO_2 /Al_2O_3 composite oxide layer and an inner Al_2O_3 layer. The capacitance of the composite oxide film showed to be 50 % larger than that of anodic oxide films on aluminum without TiO_2 film.

(5) Anodic oxide film formation after the destruction by laser irradiation.

Aluminum specimens covered with barrier type anodic oxide films with different thicknesses were irradiated with one pulse of YAG-laser under anodic polarization in a neutral boric acid/borate solution to follow the oxide film formation at the laser irradiated area. The film formation kinetics were found to obey inverge-logarithmic growthrate law.

(6) Oxidation behavior of ultra-high temperature materials

Oxidation of SiO_2-forming materials such as Si_3N_4, SiC and $MoSi_2$ at ultra-high temperatures is being carried out. The aim is to clarify the oxidation behavior of ultra-high temperature materials. Especially, emphasis is the effects of second phases such as additives and reinforcement materials on the oxidation resistance of ultra-high temperature materials. In addition, the mechanism of accelerated oxidation in $MoSi_2$ is being investigated.

(7) Solid-state reactions between metals and ceramics

The interfacial reactions in metal / ceramic(SiC or Si_3N_4) systems at high temperatures are being investigated. The aims are to clarify the mechanism of interfacial reaction between metal and ceramic, and to estimate the maximum application temperature of metal-ceramic composites.

(8) Research on development of ultra-high temperature materials

Composites such as carbon/silicide, carbon / Si-based ceramic, refractory metal / silicide, refractory metal / Si-based ceramic, and silicide / Si-based ceramic are expected as ultra-high temperature materials having high oxidation resistance. Preparation of these composites is being carried out by a spark plasma sintering equipment, the evaluation of oxidation and mechanical properties of the composites.

Other activities

Assoc. Prof. Kurokawa attended the 4th International Symposium on High Temperature Corrosion and Protection of Materials which was organized by CEFRACOR, Univ. of Provence and EPRI and held in Les Embiez, France, on May 20-24. The paper entitled "High temperature oxidation of $MoSi_2$-WSi_2 solid solutions" was presented in the symposium. In November, Prof. Takahashi and Assoc. Prof. Kurokawa visited Melbourne, Australia to attend the 13th International Corrosion Congress, and presented papers entitled "Formation of Anodic Oxide Films on Aluminum in Boric Acid / Borate Solutions. -Effect of borate concentration and pretreatment-" and "Effect of Reinforcing Materials on High Temperature Oxidation Behavior of $MoSi_2$-Based Composites," respectively. Before the congress, Prof. Takahashi visited Prof. G. Hope, Griffith University, and Prof. P. Schwinberg, Queensland University of Technology to discuss the oxide film formation and destruction on metals and alloys. Assoc. Prof. Kurokawa also visited Prof. D.J. Young, Univ. of New South Wales to discuss the oxidation and sulfidation behavior of new materials.

Foreign researchers visited the IMSA-laboratory are Dr. M. Gattrell, NRC, Canada, in March, Dr. R. X. Oltra, Bourgogne Univ., France, in April, Dr. S. Kiat, Chenmai Univ, Thailand, in May, Dr. R. S. Alwitt, Boundary Technologies Inc., U. S. A., in May, and Prof. R. A. Oriani, Univ. of Minessota, U. S. A., in October.

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Measurement of a Trace Amount of Corrosion by a Quartz Crystal Microbalance

Masahiro Seo

Materia, **35**, 255 - 260 (1996)

A quartz crystal microbalance (QCM) is capable of detecting small mass changes in the region of nanograms per square centimeter from resonant frequency changes of a quartz oscillator. Recent utilization of metal thin films in electronic materials and devices has increased with increasing demand for data processing of high density and high speed. The corrosion of thin films, even if minute, will provide severe damage of the equipment because of the very small and limited size.

QCM is powerful for measurement of very small corrosion rate of metal thin films. This article described the principle and practical technique of QCM and introduced the typical examples of application of QCM to atmospheric and aqueous corrosion of metal thin films. (Japanese)

Microvisualization of Metal Surfaces Subjected to Corrosion

W. H. Smyrl and M. Seo

The Journal of the Surface Finishing
Society of Japan, **4**, 82 - 487 (1996)

Microvisualization of metal surfaces subjected to corrosion is important to investigate precursor sites of localized corrosion such as pitting corrosion and stress corrosion cracking. This article reviewed recent advances in optical, electrochemical and photoelectrochemical methods which will be powerful for microvisualization of metal surfaces subjected to corrosion and introduced typical examples for application of these methods. (Japanese)

Pursuit of Initiation of Localized Corrosion Using by a Scanning Electrochemical Microscope

K. Fushimi

Journal of the Surface Science Society
of Japan, **17**, 703 (1996)

Localized corrosion including pitting is the most dangerous corrosion morphology of metals and alloys. The Initiation process of localized corrosion, however, is not well understood because there are no powerful methods to evaluate the position of precursor sites and their development. This short article introduces two papers for pursuit of initiation of localized corrosion using by a scanning electrochemical microscope which is an useful tool to evaluate surface heterogeneity in mezoscopic region. (Japanese)

Corrosion Protection of Reinforced Concrete Members by Using Recycled Steel

A.Keyvani Someh,N.Saeki and T.Notoya

Proceedings of the 12th International Conference on Solid Waste Technology and Management, 5D 1-8 (1996)

Two targets included in this research. the first was recycling idea as a reusing of waste steels and the second was to protect corrosion of reinforcing concrete in a natural method. To retard or inhibit corrosion of reinforced concrete by reusing of steel shavings/or steel cans materials as steel fibers around embedded steel bars as a sacrificial anode was investigeited.

Investigation in a transparent gel and reinforced concrete specimens indicated that steel fibers results from steel cans/or steel shavings can play a role of sacrificial anode to protect corrosion of steel bars. Also, results of exposed reinforced concrete specimens under severe conditions confirmed the role of corrosion protection of above materials especially for steel cans fibers and anti-corrosion behavior was observed for embedded steel bars. (English)

Corrosion Protection of Steel Fibers on Steel Reinforced Concrete Members

A. Keyvani Someh,N.Saeki & T.Notoya

Proc. Sympo. Appl. Advanced Reinforcing. Mater. Concr. Struct.
JIC Hokkaido Chapter, 81-88(1996)

Severe deterioration caused by corroding reiforcing steel in concrete structures is a major concern in the maintenance of infrastructures under an accelerated artificial aggressive conditions, and in a normal strength concrete, the corrosion protection behavior of zinc-coated, galvanized steel fibers in reinforced concrete specimens is studied. Corrosion phenomenon in the steel fibers connected to steel bars shows a sacrificial role of fibers for steel bars. In general, the results indicate, when galvanized steel fibers and steel bars are beside each others, the initiation of corrosion occurs in the galvanized steel fibers. No corrosion results of embbeded steel bars in the steel fiber reinforced concrete matrix, show the merit of galvanized steel fibers as an alternative method to inhibit corrosion of reinforced concrete members. (English)

Simulation of Role of Steel Fibers for Corrosion Protection of Reinforced Concrete Members

A.Keyvani Someh, N.Saeki and T.Notoya

JCA Proceedings of Cemet and Concrete
No 50, 306-311(1996)

The corrosion behavior of steel fibers in steel fiber reinforced concrete has not been methodically studied as those of reinforcing steel and prestressing steel, particularly for corrosion protection of reinforced concrete. In general, the findings regarding the corrosion behavior of steel fibers have been good. Corrosion of the fiber reinforced concrete has been shown to at the surface of members, and corrosion of steel fibers inside of concrete matrix has not been essentially obeserved. In this study, a modified ferro-oxyl test was used to simulate the initiation and propagation of corrosion of steel fibers, particularly in contact with the steel bars. This test enabled observation of the electrochemical corrosion process of steel fibers and steel bars in a transparent agar gel. This technique was useful for understanding corrosion phenomena in the steel fibers and the role of steel fibers in the corrosion protection of steel bars under severe conditions. (English)

Metabolism of Pure Sulfate-Reducing Bacteria in the Presence of Ferrous Ions and Environmental Changes of the Medium

F. Baba, A. Suzuki and M. Seo

Zairyo to Kankyo (Journal of Corrosion Engineering of Japan),
45, 588 - 594 (1996)

Effects of ferrous ions on the shape and activity of sulfate-reducing bacteria (SRB) have been investigated using a phase-difference microscope, hydrogen sulfide gas detector, and measuring the amount of ferrous sulfide in the medium. SRB changed its shape at an interval of several hours as the culturing time increased. At the time of maximum activity of SRB, SRB evolved a significant amount of hydrogen sulfide and changed from rod like shape to comma like shape. After this period, pH of the medium increased above 9.0 and the size of SRB became less with reduced evolution of hydrogen sulfide. Even if some amount of HCl was added to keep pH of the medium at 7.0, the hydrogen sulfide evolution was not recovered. In the medium with high concentration (0.01 mol kg^{-1}) of ferrous ions, colloidal substance were present and seemed to provide a comfortable place for SRB to grow, ripen, and split easily. In the medium with low concentration (0.00036 mol kg^{-1}) of ferrous ions, the colloidal materials were few and the number of SRB was less than that in the high concentration (0.01 mol kg^{-1}) medium. It is concluded that ferrous ions do not only affect directly the metabolism of SRB, but also form the colloidal substance on which SRB can keep alive easily. (Japanese)

Corrosion Behavior of Carbon Steel Exposed for Long Time to an Inoculation Medium of Sulfate-Reducing Bacteria

F. Baba, A. Suzuki and M. Seo

Zairyo to Kankyo (Journal of Corrosion Engineering of Japan),
45, 595 - 602 (1996)

Carbon steel was exposed for long time to an inoculation medium of sulfate-reducing bacteria (SRB). The corrosion behavior was investigated by measuring weight loss of the specimens and by using surface-analytical methods such as EPMA. In the medium containing ferrous ions of high concentration (0.01 mol kg^{-1}), the corrosion rate of carbon steel took a maximum value. The weight loss increased linearly with time after exposure up to four weeks. The corrosion rate in the medium containing ferrous ions of 3.6×10^{-4} mol kg^{-1} and 0.3 mol kg^{-1} was not so large as that in the medium containing ferrous ions of 0.01 mol kg^{-1}. The activity of SRB as well as the corrosion rate depended strongly on the concentration of ferrous ions. The EPMA results suggested that the some area of steel surface covered with the scale would act as a cathode and the other area would act as an anode. The formation of effective cathode area was closely related to the formation of FeS and dependent on the exposed time. Even if an antibiotic was added into the medium after exposure of two weeks, the corrosion did not cease and increased linearly with time after exposure above four weeks. Thus it is found that the contribution of SRB to the corrosion is associated with the creation of corrosive environment in the initial stage of culture up to two weeks. (Japanese)

Semiconductive Properties of the Passive Films

K. Azumi and M. Seo

Denki Kagaku, **64**, 258 - 261 (1996)

Semiconductive properties of the passive films formed on iron and titanium are discussed. Potential distribution in the passive films can be estimated from the Poisson's equation for the n-type semiconductor passive films under the anodic polarization, and is related to the potential dependence of the film thickness, and the defect density acting as donor states. Structure and electronic properties are influenced by the electrolyte composition and the strength of the electric field. For example, donor density of the passive film on iron increases in phosphate solution because of anion penetration. For the case of titanium, the film structure changes from amorphous to crystalline with potential raising, and microcrystalline at higher potentials, resulting in breakdown due to very high electric field in the film. The band structure of the passive film should be connected with the various electrochemical phenomenon, such as change in valency of oxide film, charge transfer with the redox system in the electrolyte, and the charge distribution due to anion adsorption. (Japanese)

An Electrochemical and SERS Study of the Effect of 1-[N,N-bis-(hydroxyethyl)aminomethyl]-benzotriazole on the Acid Corrosion and Dezincification of 60/40 Brass

V.Otieno-Alego,G.E.Hope,T.Notoya and D.P.Schweinsberg

Corrosion Science, **38**,No 2, 213-223(1996)

The effect of 1-[N,N-bis-(hydroxyethyl)aminomethyl]-benzotriazole(BTLY) on the corrosion and dezincification of a 60/40 brass in aqueous sulfuric acid at 30°C has been investigated by means of solution analysis, potentiodynamic and surface enhanced Raman scattering (SERS) techniques. Overall inhibition for copper and zinc dissolution increased with increasing concentration to a maximum (63.1%) at the 5×10^{-4}M level. This was comparable to that observed for benzotriazole(BTAH) under the same conditions. Solution analysis indicates that BTLY is ineffective in preventing dezincification. Polarization studies show that BTLY acts initially to suppress the cathodic and anodic corrosion reactions. The SERS spectra suggest that the adsorption with copper in the brass occurs through nitrogen in the azole ring of the protonated molecule of BTLYH.(English)

Inhibition Effect of Benzotriazole and Benzotriazole-monoethanolamine on Corrosion of Copper

T.Notoya

J. Japan Copper and Brass Research Association,
35, 235-239(1996)

The inhibition of copper corrosion in buffered and non-buffered 3% NaCl solutions by benzotriazole(BTA), monoethanolamine(MEA), BTA-MEA equimolar salt(BTA-MEA), and an equimolar mixture of BTA-HCHO-MEA(BTA·MA) was assesed by means of solution analysis and potentiodynamic techniques. The inhibitive efficiency increased with increases in the concentration of BTA, BTA-MEA and BTA·MA in the range of 0.5 to 10m mol/l in buffered solutions of pH 3.6, 6.4 and 9.2, while MEA accelerated copper corrosion in solutions of pH 6.4 and 9.2. The performance of BTA was improved by a limited amount (1~2%) by mixing with MEA in the buffered solutions. The addition of MEA,however,raised pH of non-buffered solution and made them less corrosive for copper. (Japanese)

An Electrochemical and SERS Study of the Synergistic Effect of 1-[(1',2'-Dicarboxy)ethyl]-benzotriazole and KI for the Inhibition of Copper Corrosion in Aerated Sulphuric Acid

V.Otieno-Alego,S.E.Bottle,T.Notoya and D.P.Schweinsberg

Proc. 13th International Corrosion Congress,
3, paper 320, 1-8(1996)

The inhibition of copper corrosion in aerated 0.5 M sulphuric acid at 30 ℃by 1-[(1',2'-Dicarboxy)ethyl]-benzotriazole(BTM) has been assessed by means of solution analysis, potentiodynamic and surface enhanced Raman scattering (SERS) techniques. The inhibition efficiency increased with increasing BTM concentration to a maximum(52%) at the lmM level. Benzotriazole(BTAH) was found to be about 20% more efficient as an inhibitor for copper corrosion under the same conditions. BTM (l mM) showed increased inhibition with increasing pH reaching a maximum value of 78.3 % at pH=8. Polarization studies showed that BTM supressed both the cathodic and anodic corrosion reactions. The SERS studies suggest that, like BTAH, BTM inhibits copper corrosion by adsorption through the azole nitrogen. This study also showed that mixtures of BTM and potassium iodide are very efficient in protecting copper corrosion in acid solutions down to pH=3. The synergistic effect of iodide has been explained by the adsorption of iodide ions on the copper surface followed by an over layer of protonated BTM molecules to form a more compact and corrosion resisting polymeric Cu-I-BTM complex. Addition of KI caused a deterioration in the quality of the SERS spectrum and this supports the initial adsorption of iodide ions on the metal. (English)

Production of Al_3Ti by the reaction of Al with $TiCl_4$ dissolved in NaCl-KCl molten salts

Takehiko KUMAGAI, Shoichi KONDA, Takeshi SASAKI and
Tastuo ISHIKAWA

Denki Kagaku, **64**, 296-300 (1996)

Experiments were carried out for production of Al_3Ti particles through reaction between Al and $TiCl_4$ dissolved in equi-mol NaCl-KCl molten salts at 750℃. The particles were successfully produced which had a major-axis diameter range from 10 to 30μm. The following reaction path was estimated by analyzing the bulk melt composition:

$$3TiCl_4 + 4Al \rightarrow 3Ti + 4AlCl_3$$

It was found that Al alloys containing 50wt% Al_3Ti particles can be produced by the reaction at a maximum rate of $2.5A/cm^2$.(Japanese)

Measurement of Electrical Conductivity in Chloride Melts Containing AlF_3-NaF by Changing Inter-electrode Distances

Mikito UEDA, Shoichi KONDA, Takeshi SASAKI and
Tatsuo ISHIKAWA

Denki Kagaku, **64**, 978-983 (1996)

Electrical conductivity of chloride melts containing fluorides expected to be useful as an Al electrorefining bath was measured by changing distances between a graphite cathode and an aluminum- copper alloy anode. The melts were prepared by adding prescribed amounts of a 40 mol % AlF_3-NaF double salt to 40 ~ 60 mol % $BaCl_2$-NaCl solvent melts and investigated in the concentration range of AlF_3 from 5 to 15 mol%. Electric conductivities of the melts were determined to be in the region of 2.0 to 2.8 $S \cdot cm^{-1}$ at 750~850℃ and the activation energies varied from 1.9 to 2.8 $kJ \cdot mol^{-1}$. The electrical conductivity increased with an increase of AlF_3 concentration in 50 and 60 mol% $BaCl_2$- NaCl solvent melts, but it decreased in the 40 mol% $BaCl_2$-NaCl solvent melt. The increases in conductivity were due to increase in the mole fraction of Na components in the melts by the addition of 40 mol% AlF_3-NaF double salts. The cause for the decrease was also discussed in terms of the increase in complex anions derived from AlF_3. (Japanese)

Reduction Reaction of Chlorine Gas in an Al-Cl_2 Chemical Cell Composed of Molten Chloride Salts

Shoichi KONDA, Takeshi SASAKI and Tatsuo ISHIKAWA

Denki Kagaku, **64**, 1090-1096 (1996)

An aluminum-chlorine chemical cell for manufacturing aluminum chloride was proposed as one compornent process of an electrochemical cycle system for reproduction of aluminum from scrap aluminum. Graphite rods were used for the cathodes of the cell, and the performance for the reduction of chlorine was investigated in terms of the output characteristics of the cell by varying the lengths of the reaction zones and the positions of menisci through manipulation of the melt levels. The measurements were carried out in a mixture of 25mol% $MgCl_2$-75mol% NaCl and an equi-mol NaCl-KCl melt at 750℃.

On the basis of dividing the inner resistance of the cell into the reaction resistance of chlorine reduction and the electric resistance of the melts, we found that the main depression of the cell voltage was caused by the reaction resistance, though the resistance decreased with the increase in the length of the reaction zones. In the course of a raise of the meniscus levels, output current and voltage increased, whereas during lowering of the meniscus levels the values decreased compared with those of the stagnant state. These suggest that thin melt layers with higher concentration of chlorine than the bulk are formed on the graphite surfaces near the menisci. The product of the reaction resistance and the reaction zone length was nearly constant, and this relation offers a guiding principle to design a new chemical cell. (Japanese)

Characteristics of Cathodic Reactions in $BaCl_2$-NaCl Melts Containing AlF_3 Components

Mikito UEDA, Shoichi KONDA, Takeshi SASAKI
and Tatsuo ISHIKAWA

Proc. 10th Int. Symp. Molten Salts PV-96-7, 236-243 (1996)

For electrorefining of Al from scrap aluminum using a bipolar electrode system, characteristics of $BaCl_2$-NaCl melts, less corrosive for cell materials than fluoride melts, were investigated. First, methods for introducing aluminum components into $BaCl_2$-NaCl melts were examined in terms of their solubilities. Only melts fed with double salts of AlF_3-NaF were available for the electrolysis bath. Next, characteristics of cathodic reactions in the melts with various concentrations of aluminum components were investigated. Plateau currents were observed at 0.35 and 0.75A/cm^2 in 2.5 and 5mol% melts, respectively, whereas no plateau current was found in 10mol% melts. (English)

Measurement of Electrical Conductivity in $BaCl_2$-NaCl-AlF_3-NaF Melts by Changing Inter-electrode Distances

Mikito UEDA, Shoichi KONDA, Takeshi SASAKI
and Tatsuo ISHIKAWA

Proc. 6th Japan-China Bilateral Conf. On Molten Salt
Chem. And Tech., 86-89 (1996)

We have developed a technique to measure electrical conductivity of electrolytic melts in the electrorefining cell under the working state and determined the electrical conductivities of chloride melts containing fluorides by changing distances between a graphite cathode and an aluminum-copper alloy anode.

The melts were prepared by adding prescribed amounts of a 40 mol% AlF_3-NaF double salt to 40 - 60 mol% $BaCl_2$-NaCl solvent melts and investigated in the concentration range of AlF_3 from 5 to 15 mol%. Electrical conductivities of the melts were determined to be in the region of 2.0 to 2.8 $S \cdot cm^{-1}$ at 750-850℃ . They increased with an increase of the AlF_3 concentration in 50 and 60 mol% $BaCl_2$-NaCl solvent melts, but they decreased in the 40 mol% $BaCl_2$-NaCl solvent melt. The increment in conductivity was due to an increase in the mole fraction of Na components in the melts by the addition of 40 mol% AlF_3-NaF double salts. The cause for the decrease was also discussed in terms of the increase in complex anions derived from AlF_3. (English)

Effects of Reinforcing Materials on High Temperature Oxidation Behavior of $MoSi_2$-Based Composites

K. Kurokawa, H. Uchiyama, M. Ube, H. Takahashi,
and W. L. Worrell

Proc. 13th Intern. Corros. Cong., 1401-1406(1996)

This study reports the effects of the reinforcing materials such as Al_2O_3, ZrO_2, HfO_2, and SiC on high temperature oxidation behavior of $MoSi_2$-based composites. Specimens used in this study were $MoSi_2$, $MoSi_2$-20 vol.% oxide (Al_2O_3, ZrO_2, or HfO_2), $MoSi_2$-10 vol.% SiC-10 vol.% stabilized ZrO_2, and $MoSi_2$-10, 30 vol.% SiC. The oxidation tests were carried out isothermally at 1773 K in air. The $MoSi_2$-based composites, except for the $MoSi_2$-20% ZrO_2, showed excellent resistance to oxidation because of the formation of a protective SiO_2 layer. The decrease in resistance to oxidation in the composites containing ZrO_2 was due to the formation of $ZrSiO_4$ and crevice oxidation associated with the shrinkage in volume of ZrO_2 in its phase transformation. Therefore, the improved oxidation resistance can be achieved by using fully stabilized ZrO_2 which contains Y_2O_3. Al_2O_3 dissolves into an SiO_2 layer to form an oxide layer which is close to the molten state, although the influence on the oxidation rate is negligibly small. It is concluded that the reinforcing materials which little affect the formation of a protective SiO_2 layer are SiC and HfO_2. (English)

Sulfidation Behavior of Fe-Cr Alloys in Low Sulfur Pressures

Manabu Noguchi and Toshio Narita

J.Japan Inst.Metals, **60**,No.2, 198-204(1996)

Sulfidation behavior of Fe-Cr alloys containing up to 25 at%Cr was investigated under the sulfur pressures above a dissociation pressure of ferrous sulfide at temperatures of 1023,1073 and 1123 K using a thrmo-gravimetry and an electron micro-probe analysis.

The surface sulfide scale was composed of$(Fe,Cr)_{1-\delta}S$ and its growth kinetics was parabolic.The parabolic rate constants(kp)increased with increasing Cr content and sulfur partial pressure,while they showed an abnormal temperature dependence at a 10^{-3} Pa sulfur pressure.These could be due to a competitive effect of a dynamic factor(cation diffusivities) and a driving force factor(sulfur activity difference across the scale).

It was found that Cr in the scale enriched near an alloy/scale interface and then decreased gradually toward a scale/gas interface,and these cation profiles became steeper with increasing sulfur pressure.Diffusional analyses of cation distributions showed that Cr is a slower-diffusant in the$(Fe,Cr)_{1-\delta}S$ sulfide,with the D_{Cr}/D_{Fe} ratios ranging from 0.1 to 0.5.Scale structures and cation distributions could be elucidated by paths of change in composition on the Fe-Cr-S phase diagram.(Japanese)

Internal Sulfidation Properties of Fe-Cr and Fe-Mn Alloys

Shigehiro Kawamori* and Toshio Narita**

Zairyo-to-Kankyo,**45**,146 ～151(1996)

Sulfidation behavior of Fe-26 at %Cr,-36 at %Cr,and-12 at%Mn alloys at temperatures of 1073 and 1173 K was investigated at a sulfur pressure lower than the dissociation pressure of ferrous sulfide at each temperature.External sulfide scales of $(Cr,Fe)_3S_4$ or(Mn,Fe)S were formed with or without formation of an internal sulfide.The general internal sulfidation appeared for the Fe-Mn alloy at both temperatures and the latter was due to an α to γ phase change.The sulfidation of an Fe-26 at%Cr alloy at 1073 K was confined within grain-boundaries.This was caused by a high sulfur solubility there.A mixture of general and grain-boundary sulfidation appeared when the Fe-36 at%Cr alloy was sulfidized at 1173 K.The internal sulfidations of general,grain-boundary and their mixtures were explained by applying the criterion for external or internal oxidation proposed by Wagner.(Japanese)

Nonstoichiometry in Iron-Chromium Sulfide(Fe-Cr)$_{1-\delta}$S at High Temperatures

Manabu Noguchi and Toshio Narita

J.Japan Inst.Metals,**60**,No.6, 589-594(1996)

Deviation from stoichiometric composition of ferrous-sulfide Fe-$_{1-\delta}$S and solid solution sulfides(Fe,Cr)$_{1-\delta}$S containing Cr up to 0.3 cation fraction was measured as functions of sulfide composition ζ ,sulfur pressures(1~10^{-5}Pa)and temperatures(973 ~1173K)using a thermogravimetric technique.

Nonstoichiometry δ increased with increasing Cr content in the(Fe,Cr)$_{1-\delta}$S and sulfur pressures,while it decreased with increasing temperature at a constant composition and sulfur pressure.Cation vacancy is a predominant lattice defect in the(Fe,Cr)$_{1-\delta}$S sulfide,and from the Libowitz model nonstichiometry δ and sulfur activity a_s could be expressed by the following relation:

$$\ln\left(\frac{a_s}{\delta}\right) = \frac{\mu_{MeS} + q_{VMe}}{RT} + \frac{4\sigma_{VFe}\,\delta(2-\delta)}{RT}$$

where μ_{MeS} is a free energy change for formation of a sulfide with stoichiometric composition as well as q_{VMe} and σ_{VMe} are the formation and interaction energies of cation vacancies.It was observed that values of σ_{VMe} were positive,ranging from 50 to 70 kJ/mol,independent of sulfide compositions,and the values of q_{VMe} decreased from 56 to 17 kJ/mol with increasing sulfide composition.(Japanese)

Effect of a Small Amount of Hydrogen Chloride on High Temperature Oxidation of Iron-Chromium Alloys

Yoshiyuki Sato[*],Motoi Hara[*],
Yutaka Shinata[*††] and Toshio Narita[**]

J.Japan Inst.Metals,**60**,No.9, 841-847(1996)

High temperature oxidation behavior of Fe-1,2,5 and 18 mass%Cr alloys was examined by thermogravimetry in 1%HCl-50%O_2-N_2 and 100%O_2 atmospheres at temperatures between 973 and 1173K.Corrosion products were analyzed by XRD and EPMA.The mass gain of Fe-Cr alloys increased with time and temperature,and it decreased with the Cr content in the alloys.The mass gains for Fe-Cr alloys at various temperatures in a 1%HCl-50%O_2-N_2 atmosphere were larger than those in 100%O_2,while the Cr content dependence of mass gains of Fe-Cr alloys in 1%HCl-50%O_2-N_2 had almost the same tendency as that in 100%0_2.Namely,the mass gain decreased with the Cr content of the alloy and the 18 mass% addition of Cr was effective to reduce the corrosion rate.In the 1%HCl-50%O_2-N_2 atmosphere,the scale formed on Fe-5%Cr alloy consisted of two layers of thick and dense Fe oxides and a porous Fe-Cr spinel oxide($FeCr_2O_4$).The scale formed on the Fe-18%Cr alloy was a single layer of Fe oxides with segregation of Cr_2O_3 in the bottom part of the scale.From the results obtained and a thermodynamic discussion,it was suggested that the accelerated oxidation was due to the formation of volatile $FeCl_2$ in addition to the oxidation of Fe and Cr,and that the Cr addition to the alloy led to reduce the corrosion rate because of the formation of a protective $FeCr_2O_4$ layer or a Cr_2O_3 layer in the scale.(Japanese)

Effect of a Small Amount of Hydrogen Chloride on High Temperature Oxidation of Nickel-Chromium Alloys

Yoshiyuki Sato*,Motoi Hara*,
Yutaka Shinata*†† and Toshio Narita**

J.Japan Inst.Metals,**61**,No.1, 56-63(1997)

High temperature oxidation behavior of Ni-5,10 and 20%Cr alloys in a 1%HCL-50%O_2-N_2 atmosphere was examined at 973-1273 K by thermogravimetry.Mass gains of the Ni-5 and 10%Cr alloys in the 1%HCl-50%O_2-N_2 atmosphere increased with time in the early stage of the reaction and then decreased to show negative values.On the other hand,mass gain of Ni-20%Cr alloy decreased with time from the early stage.Total metal consumptions of these alloys showed a simple increase with time and with oxidation temperature.To investigate the mechanism of the reaction taken place at the stated conditions,the metal consumptions were divided into two kinds of consumption,i.e.consumptions for oxidation and chlorination .The metal consumption for oxidation increased with time in the earlier stage,and then showed a nearly constant value.In another hand,the metal consumuption for chlorination appeared very small values at first,and then showed a constant rate at the later stage.Scales formed on Ni-5 and 10%Cr alloys consisted of NiO,and an elemental Cr was detected in them.In the scales formed on Ni-20%Cr alloys,Cr_2O_3 was identified .From all the results and a thermodynamical equilibrium discussion,it was revealed that oxidation and chlorination reactions took place simultaneously in the 1%HCl-50%O_2-N_2 atmosphere at high temperatures.It was also found that the addition of 20%Cr effectively reduced oxidation and chlorination in the HCl-bearing atmosphere.(Japanese)

Improvement of Oxidation Resistance of TiAl Intermetallic Compound by Sulfidation Treatment

Takayuki Yoshioka* and Toshio Narita**

Zairyo-to-Kankyo,**45**,712-716(1996)

The oxidation resistance was investigated in air at 1173K for the TiAl alloy,which has been pre-sulfidized at 1173K in a H_2-H_2S gas mixture to form a $TiAl_3$ layer on the alloy surface due to selective sulfidation of Ti,and changes of the $TiAl_3$ into $TiAl_2$ phase as well as their effects on oxidation behavior were considered.

It was found that the pre-formed $TiAl_3$ layer with 20 μm thickness was changed into a $TiAl_2$ layer after oxidation at 1173K for 86.4 ks. Both the $TiAl_3$ and $TiAl_2$ layers indicated very good oxidation resistance for long time,up to 810 ks.These two layers showed re-passivation capability a protective Al_2O_3 Scale.(Japanese)

Initial Oxidation of Type 430 Stainless Steel in O_2-H_2O-N_2 atmospheres at 1273 K

Isao SAEKI, Hidetaka KONNO, Ryusaburo FURUICHI

Corrosion Science, **38**, 19-31(1996)

Initial oxidation of type 430 stainless steel was studied in O_2-H_2O-N_2 atmospheres at 1273 K up to 180 s. The morphology of the oxide films changed with oxidation time. Isolated oxide particles grew in the initial 30 s, then the particles started to merge, but compact film was not formed even after 120 s oxidation. The oxidation rate was high until 30 s and then decreased, but did not fit any oxidation rate law. Films were composed of only corundum type $(Fe,Cr)_2O_3$ oxide. The surface and bulk concentration of both Fe and Cr ions changed in the initial 30 s, and then reached steady values. The oxides were found to orient along the c-axis of the hexagonal cell after 30 s oxidation. Morphology, composition, structure and growth rates were not affected by the oxidizing atmosphere, but the preferred c-axis orientation was enhanced with high P_{H_2O}.

Initial Oxidation of Type 430 Stainless Steels with 0.09-0.9 Mn in O_2-N_2 atmosphere at 1273 K.

Isao SAEKI, Hidetaka KONNO, and Ryusaburo FURUICHI

Corrosion Science, **38**, 1595-1612(1996)

Initial oxidation of type 430 stainless steels with Mn (0.09, 0.38, and 0.9 mass %) was studied in 0.165 atm O_2-N_2 atmosphere at 1273 K. For 0.09Mn steel, only corundum type oxide was formed. Initially the oxide film was rich in Fe and the Cr concentration in the oxide increased with oxidation time until 30 s when the film composition became constant. The oxidation behavior of the 0.38 and 0.9Mn stainless steels was similar to that of 0.09Mn steel until 30 s, but after 30 s it became different: Mn(II) was detected at the film surface and spinel type oxide which was nucleated from pre-existing corundum type oxide appeared simultaneously. Between 30-300 s, the oxide composition and growth mechanism changed and finally the oxidation behavior reached a steady state. Different models of the oxidation processes are proposed for type 430 stainless steels with different manganese contents.

The photoelectrochemical response of TiO_2-WO_3 mixed oxide films prepared by thermal oxidation of titanium coated with tungsten.

Isao Saeki, Naoya Okushi, Hidetaka Konno,
and Ryusaburo Furuichi

J. Electrochem. Soc.,**143**, 2226-2230(1996)

Titanium sheets coated with vacuum deposited tungsten films were oxidized at 1073 and 1173 K to form TiO_2-WO_3 mixed oxide films. The mixed oxide films showed higher anodic photocurrents than pure TiO_2 films formed on Ti due to the oxidation of water. The photocurrent increased with the amount of W deposition on Ti substrate and with oxidation temperature. From SEM, XRD, and XPS experiments, it is concluded that the films containing larger amounts and uniformly distributed W in the depth direction of the film generate larger photocurrents. For WO_3 films formed by thermal oxidation of W sheets, there was anodic dissolution of the underlying metal. This may be due to imperfections in the WO_3 film. Such dissolution was not observed for the TiO_2-WO_3 mixed oxide films, showing the electrochemical stability of these films.

Piezoelectric Detection of Changes in Surface Energy of Gold Electrode in Perchlorate Solutions Containing Iodide Ions

M. Seo and K. Ueno

Journal of the Electrochemical Society,
143, 889 - 904 (1996)

The changes in surface energy of a gold electrode in deaerated 1.0 mol dm^{-3} $NaClO_4$ solutions with and without iodide ions were sensitively detected by using a piezoelectric technique. The potential of zero charge (pzc) of gold electrode was evaluated from the piezoelectric signal curve. The addition of iodide ions shifted significantly pzc to the negative direction, indicating the strong contact adsorption of iodide ions. It was found from the iodide concentration dependence of pzc that the Esin- Markov relation held at pzc. The piezoelectric signals at the high potentials far from pzc suggested the possibility of structural changes or phase change of iodine adlayer with sign reversal of total surface charge density. (English)

Influence of HF Concentration and Specific Resistivity of Substrate on Microstructure and Luminescence Behavior of Porous Si

K. Shigyo, M. Seo, K. Azumi, H. Takahashi,
M. Al-Odan and W. H. Smyrl

The Journal of the Surface Finishing Society of Japan,
47, 157 - 162 (1996)

A porous silicon layer (PSL) was prepared on single crystal p-type Si (100) wafers with electrochemical etching in HF aqueous solutions of various concentrations to explore the optimum PSL preparation conditions for no exfoliation of the PSL from the substrate and for good reproducibility of visible luminescence with high intensity. The surface morphology and microstructure of the PSL were observed using various microscopic techniques (SEM, TEM and CLSM) and the surface compound of PSL was identified by FT-IR. In addition to the photoluminescence (PL), the electroluminescence (EL) emitted from the PSL during anodic oxidation in KNO_3 aqueous solution was measured to examine the luminescence mechanism. The microstructure of PSL prepared on Si with low specific resistivity (ρ $=0.1\,\Omega$m)was columnar, whereas that prepared on Si with high specific resistivity ($\rho=1$kΩm) was granular and randomly oriented. The microstructure of PSL also changed depending on the HF concentration. The EL and PL intensities of PSL were both higher for $\rho=1$kΩm than for $\rho=0.1\,\Omega$ m and increased with decreasing HF concentration. The exfoliation of PSL from the substrate of $\rho=1$kΩm was prevented by using low current density in electrochemical etching. The optimum PSL preparation conditions were finally obtained when the specimen with specific resistivity of $\rho=1$kΩ m was electrochemically etched in 10.4 wt% HF aqueous solution under a galvanostatic condition of i = 10 A m^{-2} for 15 ks. The TEM images of PSL with high magnification (5 x 10^5) suggest that the quantum confinement effect is operative in the visible luminescence. (Japanese)

Influence of Electrochemical Etching Current Density on Porous Si Luminescence Properties and Microstructure

K. Shigyo, M. Seo, K. Azumi and H. Takahashi

The Journal of the Surface Finishing Society of Japan,
47, 949 - 956 (1996)

A porous silicon layer (PSL) was prepared on single-crystal p-type Si(100) wafers with electrochemical etching in HF solutions at different current densities to explore the effect of current density on the PSL luminescence properties and microstructure. Luminescence was evaluated by measuring photoluminescence (PL) spectra. The microstructure was observed using FE-SEM, TEM, and CLSM. The surface composition was determined using FT-IR analysis. The PL intensity emitted by the PSL increased with increasing electrochemical etching current density. TEM images indicated that the PSL prepared on a Si specimen with a specific resistivity of 1 kΩm consisted of dispersed ultrafine Si particles with a diameter of 2 - 5 nm. The structure of the PSL prepared on a Si specimen with a specific resistivity of 0.1 Ωm was coarse and columnar. The PSL microstructure (0.1 Ωm) became fine and granular with increasing current density. FT-IR spectra showed that the surface SiH_X concentration of PSL decreased with increasing current density. From these results, we concluded that the quantum confinement effect is operative on the visible luminescence from the PSL, and the surface compound consisting of SiH_X forms surface states reducing the luminescence intensity. The electronic band models of the SiH_X/PSL/p-Si substrate are proposed to explain the visible PL mechanism. (Japanese)

Formation of Anodic Oxide Films on Aluminumin Boric Acid / Borate Solutions-Effect of borate concentration and pretreatment-

Y. Li, H. Shimada, K. Shigyo, M. Sakairi, H. Takahashi, and M. Seo

Proc. 13th Intern. Corros. Congr., 528 - 533 (1996)

Highly pure aluminum was anodized at a constant current density of 25 A m^{-2} at 293 K in 0.5 kmol m^{-3}-boric acid / (0, 0.005 or 0.05) kmol m^{-3}-sodium tetraborate solution to examine the effect of sodium tetraborate concentration on the formation and breakdown characteristics of barrier oxide films, by using inductively coupled plasma atomic emission spectrometry, electroluminescence (EL) / photoluminescence (PL) measurements, scanning electron microscopy, transmission electron microscopy, and electrochemical impedance spectroscopy. The effect of hydrothermal treatments in pure water and an ethyl amine solution on the film formation during anodizing in a boric acid solution has been also examined.

In boric acid / borate solutions, dense amorphous anodic oxide films with smooth surface grew until film breakdown starts at 420 - 540 V. In the intermediate region of anodic oxide films, crystalline alumina with voids was found locally in the intermediate region of anodic oxide films. The EL was observed only after film breakdown.

In the boric acid solution, an amorphous oxide film grew until 1180 V with the formation and development of imperfections, and the electroluminescence and gas evolution became pronounced as the potential increased. At imperfections, the oxide / solution interface was convex and oxide / metal interface curved in the opposite direction. The breakdown of the oxide film started when the O_2 evolution and oxide dissolution at imperfections become predominant.

Boiling in pure water and ethyl amine solutions increased in the rate of increase in anode potential during anodizing considerably, and decreased the breakdown potential slightly. Crystalline oxide layers were found in the intermediate region of anodic oxide films formed after boiling, and the development of the crystalline oxide layer was more remarkable for the specimen boiled in pure water than in the amine solution. (English)

The Front of Investigation on Anodizing.
- Anodic Oxide Films on Aluminum for Electrolytic Capacitor -

H. Takahashi, M. Sakairi, H. Kamada, and M. Shikanai

Kagaku Kogyo, 44, 951 - 958(1996)

The role of anodic oxide films on aluminum in electrolytic capacitors is described, and a couple of methods are introduced for the enhancement of the relative dielectric constant of the anodic oxide films, using pore-filling and CVD/anodizing.

In the pore-filling, porous type anodic oxide films were formed on aluminum and the specimen was immersed in an acid solution to wide the pore-radius. After pore-widening, Ti-oxide was deposited on the inner wall of pores by dipping Ti^{4+}ion containing solution and by heating. The specimen was then re-anodized in a neutral boric acid / borate solution to form composite oxides in the pore. The composite oxide films produced thus up to 400 V showed 40% larger in capacity than the anodic oxide film formed by reanodizing without the deposition of Ti-oxide.

In the CVD/anodizing, specimens were coated with Ti-Oxide by MOCVD, and anodized in a neutral boric acid / borate solution. Alumina layer and Al-Ti composite oxide layer were formed at the interface between Ti-oxide layer and the metal substrate during anodizing. The capacity of the composite oxide films obtained by anodizing up to 300 V showed 50 % larger than that of anodic oxide films formed on electropolished specimens. (English)

EVALUATION OF IMPERFECTIONS IN ANODIC OXIDE FILMS ON ALUMINUM BY PIT FORMATION TECHNIQUE WITH CATHODIC POLARIZATION

H. Takahashi, K. Fujiwara, F. Takashima, M. Seo, M. Al-Odan, and W.H. Smyrl

Proc. Intern. Symp. on Plant Aging and Life Predictions
of Corrodible Structures, 647 -653, (1996)

Highly pure aluminum specimens covered with barrier-type anodic oxide films were cathodically polarized in neutral solutions by potential scanning to follow the time-variation in the cathodic current, and in the amount of dissolved Al3+ ions. The film structural change during cathodic polarization was examined by scanning electron microscopy, confocal laser scanning microscopy, phase detection interferometric microscopy, and atomic force microscopy.

During cathodic polarization, pit growth was observed by the local breakdown of oxide films and dissolution of the metal substrate. The pit formation behavior was strongly dependent on the film structure and pH-buffering ability of solution, and the precursor of the pit was suggested to be imperfections in anodic oxide films.

The cathodic polarization is proposed as a technique for the evaluation of the imperfection in the anodic oxide film. (English)

Insitu IR-RAS Investigation of Surface Layers Initially Formed on Copper and Low Carbon Steel in Nitrogen or Air Containing Water Vapor and SO_2

T. Sasaki, T. Itoh, J. Itoh and T. Ishikawa

Proc. 13th ICC, 215-220 (1996)

Pure copper and low carbon steel in gaseous corrosion environments containing water vapor with 65% and 80% relative humidities (RH) and 10 ppm SO_2 were investigated using in situ infrared reflection absorption spectroscopy (IR-RAS). In the nitrogen gas carrier only a water layer was observed on copper within 30 minutes and no evidence of corrosion was found. Copper sulfite and sulfate complexes accompanying water molecules were formed in the air carrier. On low carbon steel in the nitrogen carrier iron sulfite complexes with water were observed. In the air carrier, iron sulfite and sulfate complexes were produced and something like Green Rust II were also observed. The layers mentioned above grew obeying the parabolic rate law in the experimental exposure time. (English)

In situ IR-RAS Investigation of Surface Layers Initially Formed on Metal Surfaces in Atmospheric Corrosion Environments

Takeshi Sasaki, Mamoru Nakata,
Takahiko Itoh and Tatsuo Ishikawa

Zairyo-to-Kankyo, **45**, 152-157(1996)

An in situ infrared reflection absorption spectroscopic technique was developed to investigate metal surfaces during atmospheric corrosion. Sufficient purging of the whole measurement systems with nitrogen gas, strictly constant flow rates of corrosive gases, and reciprocal measurements with p- and s-lights, together with careful optical arrangements, have enabled acquisition of spectra of water and corrosion products from thin surface layers.

Pure copper and low carbon steel were tested at room temperature. The corrosive gases containing water vapor with 65% and 80% relative humidities and 10 ppm SO_2 were introduced into the test cell by nitrogen gas or air synthesized from nitrogen and oxygen. The measurements were carried out under the passage of the gases over the specimens..

In using nitrogen as a carrier, only water layer was recognized on copper and the thickness attained a constant value within 30 minutes, whereas in corrosive gases with air as a carrier, sulfite and sulfate together with water bands were observed. On low carbon steel, sulfite and water layers were detected in the nitrogen carrier, and in using air as a carrier, bands attributed to sulfate and probably due to Green Rust II were observed together with sulfite and water bands. These layers grew obeying the parabolic rate law. (Japanese)

Measurement of Sound Velocity Near a Crack by an Acoustic Microscope

Isao ISHIKAWA,Yukio OGURA,Satoshi IKEDA,
Motohiro SUGANUMA and Toshio NARITA

Non-destructive inspection, **45**,
No.10, 749-755(1996)

By using a slit-type acoustic lens,noisy interference fringe patterns near an interface can be eliminated,and a local measurement of the sonic wave velocity becomes possible.Based on this idea,the wave velocity was measured at a place near a crack which was generated on a surface of sintered zirconia specimen during machining.It was found from the results that there existed narrow areas of ca.5μm in width along both edges of the crack,which exhibited a different sonic contrast compared to those of adjaccent areas,and that the wave velocities drastically changed there.The features described above agree well with those of a local plastic deformation zone characterized by a Laser-Raman-probe method in the phase transformation t-ZrO_2 to m-ZrO_2.(Japanese)

Changes in Aluminum Alloy Potential and Weight During the Double-Zincate Process

K. Azumi, M. Seo and L. Nanis

The Journal of the Surface Finishing Society
of Japan, **47**, 529 - 535 (1996)

We studied the mechanism behind the double-zincate process, used for pretreating aluminum alloy, through SEM observation, electrode potential tracing, and weight changes determined during each zincate process. Zinc particles grew during the first zincate process, with a thin, uniform Zn layer forming during the second zincate process. We found that the difference in zinc particle nucleation between the first and second processes is related to surface morphology and in thickness non-uniformities in the preexisting oxide film air-formed on the alloy. (Japanese)

Effect of Solution Composition on Double Zincate Process of Aluminum

K. Azumi, Y. Fujishige, M. Seo,
L. Nanis, H. Nakao and K. Tashiro

The Journal of the Surface Finishing Society
of Japan, **47**, 802 - 807 (1996)

The double-zincate processing of aluminum in three different zincate solutions was examined to evaluate the effect of solution composition. Higher concentrations of NaOH and ZnO in zincate solution dissolve both the Al oxide layer and Al substrate more rapidly. This leads to faster Zn deposition. In a solution containing Fe^{3+} ions, Fe codeposition resulted in the growth of rather small, non-hexagonal Zn particles during the first zincate process. In the second zincate process, a stratiform Zn layer grows to cover the Al substrate in a zincate solution without Fe^{3+} ions. Granular Zn is deposited due to Zn growth suppressed laterally by the codeposition of Fe in a solution containing Fe^{3+} ions. Such granular Zn deposition provides a sufficient anchor effect for subsequent electroless Ni plating. (Japanese)

Interfacial Reaction in Joining of $MoSi_2$ to Graphite by SPS Method

Tetsushi Horibe, Hajime Uchiyama and Kazuya Kurokawa

Maters. Trans. JIM, **37**, 743-747(1996)

Interfacial reaction between $MoSi_2$ and graphite in joining process using a spark plasma sintering equipment (SPS) was studied. Joining was carried out at 1673, 1873 and 2073 K for 1.2, 2.4, 3.6, and 7.2 ks. The specimens joined by SPS were evaluated by using the four-point bending strength method. Reaction zone formed at the interface was characterized by SEM, EPMA and XRD. In addition, the suppression of interfacial reaction by interposing a titanium foil between graphite and $MoSi_2$ was also done. As a result of the solid-state reaction between graphite and $MoSi_2$, SiC and Mo_5Si_3C are formed at the interface. The morphology of SiC changes from island to layer with joining time and temperature. The maximum flexural strength tends to decrease as SiC layer grows. When interposing a titanium foil, a titanium carbide layer is formed to suppress the formation of SiC. (English)

Effect of Heating Rates in Brazing on Fracture Strength of Si_3N_4/Ni Joints

Katsumi Miyama*,Masaya Ito* and Toshio Narita**

J.Japan Inst.Metals, **60**,No.5, 497-503(1996)

Silicon nitride ceramics were brazed to nickel sheet by active brazing with nickel-copper-titanium solder under various heating rates.Properties of the reacted products were analyzed by using a scaning electron microscope,an electron probe microanalyzer,an X-ray diffraction meter,and a transmission electron microscope. Joining strength was measured at the whole interface between ceramic and metal,fracture partially propagated into the ceramic in the case of the highest heating rate.The fracture occurred in the reacted products formed at the interface between silicon nitride and the nickel-copper-titanium solder.As a result of electron probe microanalysis of the reacted products on the metal-side fracture surface,silicon was detected with aluminium and oxygen,which serve as the sintering aid of silicon nitride.The silicon intensity of the reacted products increased with increasing joining strength.However,as a result of X-ray diffraction,titanium nitride in the form of a crystalline phase was detected,but no silicon compounds were detected.These results suggest that silicon in the reacted products exists as the amorphous phase with aluminium-oxide in the grain boundary of silicon nitride.

It is considered that the titanium nitride and the silicon-aluminium oxide amorphous phase are both formed as the reacted products between silicon nitride and nikel-copper-titanium solder,and the silicon-aluminium oxide amorphous phase substantially controls joining strength.(Japanese)

THE EFFECT OF CERAMIC STRENGTH ON THE FRACTURE STRENGTH OF Si_3N_4 CERAMIC-METAL JOINTS

Shohei HATA* and Toshio NARITA

Interface Science and Materials Interconnection
Proceedings of JIMIS-8,
The Japan Institute of Metals, 535-538(1996)

Abstract:Silicon nitride ceramics with nominal fracture strengths of 800,1100,and 1500MPa were joined to low thermal expansion alloys(MGA93,MGA50)using a Ag-Cu-Ti or Ni-Cu-Ti brazing alloy and a Ni/W/Ni interlayer.Ceramic/ceramic joints were also made using both the brazing alloys.Four-point bending tests showed that the fracture strengths of the ceramic/metal joints increased proportionally to the reduction in the Ni interlayer thickness,to 600Mpa for the Ag-Cu-Ti brazed joints,and to 400Mpa for the Ni-Cu-Ti brazed joints.Fracture strengths and Ni thickness dependence for all joints were independent of the ceramic strength,except for the ceramic/Ag-Cu-Ti/ceramic strengths.Fracture strength of the joints was maximized by the strength of the reaction layer,but not by the ceramic strength,and insertion of a Ni interlayer affects fracture strength due to changes in thermal residual stresses.(English)

Change in Fatigue Properties of Silicon Nitride Ceramics and Metal Joints with Thermal Cycling

Toshio Narita,Shigenari Hayashi and Shohei Hata

J.Japan Inst.Metals, **60**,No.9, 884-889(1996)

Metals of Ni or Cu joined to Si_3N_4 ceramics with Ag-or Ni-brazing filler(Ag-Cu-Ti and Ni-Cu-Ti)were thermally cycled in vacuum between room temperature and the temperatures of 573,723 and 873 K,and then the surface distortion and fracture strength of the joints were measured using scanning acoustic microscopy and a fourpoint bending test.

In the case of the RT-573 K cycling there was little change in the joints,whereas Ni and Cu metals swelled at both of the RT-723 K and RT-873 K cycles and Ni swelling was much larger than that of Cu due to Ni plate sliding at the Ag-rich layer formed within the brazing filler.The fracture strength decreased significantly after the thermal-cyclings,because of the crack formation near the ceramic/filler interface.

In the case of the Si_3N_4/Ni joint the Ni metal shrank at the early stages of the thermal cycling and then it tended to swell with the crack formation near ceramic-filler interfaces.The integrity of ceramic/metal joints could be controlled by the mechanical properties of metal components at the elevated temperatures.(Japanese)

Activation Energy for Diffusion of Cesium in Compacted Sodium Montmorillonite

Tamotsu KOZAKI, Hiroki SATO, Atsushi FUJISHIMA,
Seichi SATO and Hiroshi OHASHI

J. Nucl. Sci. Technol., **33**, No. 6, 522-524(1996)

For safety assessments of geological disposal of high-level radioactive wastes, it is important to study the migration behavior of radioactive nuclides in compacted bentonite. In the present study, the apparent diffusion coefficients and activation energies of diffusion were determined for cesium ions in compacted montmorillonite, a major clay mineral in bentonite. The activation energies obtained in the present study were 32.9 to 52.9 kJ mol^{-1}, clearly higher than for the diffusion of cesium ions in free water, 16.2 kJ mol^{-1}. The activation energies for Na-montmorillonite specimens with dry densities of 1.0, 1.2, and 1.4 x 10^3 kg m^{-3} were similar at approximately 34 kJ mol^{-1}. When the dry density of the Na-montmorillonite specimens increases, the activation energy also increases, reaching 52.9 kJ mol^{-1} at 1.8 x 10^3 kg m^{-3}. These findings suggest that the cesium in the compacted Na-montmorillonite diffuses with a different process from that in free water. (English)

Oxidation of Pyrite in Bentonite and Its Effects on Corrosion Behavior of Overpack Material

Tamotsu Kozaki, Hideki Kawabe, Hideaki Tamai, Seichi Sato,
Hiroshi Ohashi, Jitsuya Takada and Hirotake Moriyama

Radioactive Waste Research, **3**, No.1, 33-40(1996)

As a basis for safety assessments of geological disposal of high-level radioactive waste, the oxidation behavior of pyrite during drying of bentonite was studied. There was a decrease in the quantity of pyrite in the bentonite during the drying, together with a decrease in pH, and an increase in SO_4^{2-} concentration in bentonite-water suspension. These results indicate that the oxidation of pyrite proceeded gradually during the drying process.

Corrosion experiments were carried out using bentonite specimens with different drying periods to evaluate the effects of oxidation of pyrite on the corrosion rates of iron and the apparent diffusion coefficients of the corrosion products. Chemical analysis of the corrosion products was also performed using 1,10-phenanthrolin as a colorimetric indicator. It was found that the corrosion rates and the apparent diffusion coefficients increased with the drying period, and Fe^{2+} was considered to be predominant in the diffusion of the corrosion products. It is likely that the decrease of pH caused by the oxidation of pyrite affects the corrosion rates of iron and the apparent diffusion coefficient of the corrosion products in the compacted bentonite. (Japanese)

Migration Behavior of Cesium in Compacted Sodium Montmorillonite

Tamotsu Kozaki, Hiroki Sato, Atsushi Fujishima,
Seichi Sato and Hiroshi Ohashi

Radioactive Waste Research, **3**, No.1, 25-31(1996)

For safety assessments of geological disposal of high-level radioactive wastes, it is important to study the migration behavior of radioactive nuclides in compacted bentonite. In the present study, the apparent diffusion coefficients and activation energies of the diffusion were determined for cesium ions in compacted montmorillonite, a major clay mineral in bentonite. The activation energies obtained in the present study were 32.9 to 52.9 kJ mol^{-1}, clearly higher than that for the diffusion of cesium ions in free water, 16.2 kJ mol^{-1}. The activation energies for Na-montmorillonite specimens with dry densities of 1.0, 1.2, and 1.4×10^3 kg m^{-3} were similar at approximately 34 kJ mol^{-1}. When the dry density of the Na-montmorillonite specimens increases, the activation energy also increases, reaching 52.9 kJ mol^{-1} at 1.8×10^3 kg m^{-3}. These findings suggest that the cesium in the compacted Na-montmorillonite diffuses with a different process from that in free water.

Basal spacings were determined using X-ray diffraction for water-saturated, compacted Na-montmorillonite specimens. Three-water layer hydrate in the interlamellar space was observed for the Na-montmorillonite with dry densities of 1.0, 1.2, and 1.4×10^3 kg m^{-3}, where the activation energies for the diffusion were nearly constant. Only the two-water layer hydrate was found in the Na-montmorillonite with dry densities of 1.6 and 1.8×10^3 kg m^{-3}, in which the activation energy increases with the dry density. It is possible that the basal spacing could affect the migration behavior of cesium in compacted Na-montmorillonite. (Japanese)

Study on corrosion behavior of iron in bentonite using activated iron foil

Tamotsu Kozaki, Yuji Imamura, Hideaki Tamai,
Hideki Kawabe, Seichi Sato, Hiroshi Ohashi, Jitsuya Takada
and Hirotake Moriyama.

Proceedings of the Scientific Meeting of
the Research Reactor Institute,
Kyoto University,Kumatori-cho, **30**, 49-54(1996)

For performance assessment of the geological disposal of the high level radioactive waste, it is necessary to study corrosion behavior of overpack materials in compacted bentonite. In this study, a neutron-activated iron foil was used to determine corrosion rates of iron and apparent diffusion coefficients of iron corrosion products in the compacted bentonite. Average corrsoion rates and apparent diffusion coefficients obtained were from 1.5×10^{-6} to 1.0×10^{-5} m y^{-1} and from the lower limit of detection($< 2.8 \times 10^{-14} m^2 s^{-1}$) to $1.3 \times 10^{-12} m^2 s^{-1}$, respectively. Chemical analysis of the corrosion products was carried out using 1,10-phenanthrolin as a colorimetric indicator so as to obtain the concentration profiles of both Fe^{2+} and total Fe and of the Fe^{2+}/total Fe ratio. In addition, the effects of oxidation of pyrite on the corrosion and the diffusion were studied from the results of experiments using bentonite specimens with different degrees of oxidation of pyrite. It was found that the oxidation of pyrite increases both the corrosion rates and the apparent diffusion coefficients and decreases the Fe^{2+}/total Fe ratio. (Japanese)

Complexation Thermodynamics of Sr(II) and Humic Acid

Mohammad Samadfam, Yoshinobu Niitsu,
Seichi Sato and Hiroshi Ohashi.

Radiochimica Acta **73**, 211-216 (1996)

The stability constants of Sr(II)-humate complexes were determined by Schubert's ion exchange method at pH 5.0 and ionic strength 0.1. The logarithmic stability constants decreased with increasing temperature from 3.97 at 283 K to 2.95 at 313 K. The ligand to metal ratio, i, decreased similarly from 1.4 to 1.1 in the same temperature interval. Values of i larger than unity suggest that two kinds of Sr-humate complex, SrHA and $SrHA_2$, are likely formed under these experimental conditions; the logarithmic stability constants, $\log\beta_1$, and $\log\beta_2$, are 2.64 and 4.68, at 298 K. On the basis of the findings and the temperature dependence of the measured stability constants, the thermodynamic functions (ΔG, ΔH, and ΔS) of the complexation reaction of Sr ions at dilute concentrations with humic acid were determined. At 298 K, the values of ΔG, ΔH, and ΔS for SrHA complexation were -15.0 kJ eq^{-1}, -1.5 kJ eq^{-1}, and 45.3 J eq^{-1} K^{-1}, respectively, and the corresponding values for $Sr(HA)_2$ were -26.7 kJ eq^{-1}, -13.3 kJ eq^{-1}, and 45.0 kJ^{-1} K^{-1}.(English)

Thermodynamic Properties of Water in Compacted Sodium Montmorillonite

Yuji Torikai, Seichi Sato and Hiroshi Ohashi

Nuclear Technology, **115**, 73-80 (1996)

Compacted bentonite is a promising material as an engineering barrier to enclose nuclear waste. The migration of nuclides occurs in the water of bentonite, where the major mineral is sodium montmorillonite. To determine the thermodynamic properties of water in compacted sodium montmorillonite, the equilibrium vapor pressure of the water in the montmorillonite was measured as a function of water content and temperature, without external pressure.

The thermodynamic properties depend on water content but not on the dry density of unsaturated specimens. In montmorillonite, single-layer adsorption may proceed from 0 to 16 wt% water content, two-layer adsorption from 16 to 27 wt%, and three-layer adsorption above 27 wt% ; pore water appears only in the last region. It is probable that 30 wt% of the total water included in saturated montmorillonite is not in the interlayer between platelets at 45.0 wt% water content and 0.8×10^3 kg/m^3 dry density. There is a very slight amount of water, which is not bound between platelets at dry densities of 1.20 and 1.76×10^3 kg/m^3. This water is not a dilute electrolytic solution but has higher ionic strength, like typical seawater of salinity 23‰ and saturated NaCl. (Engish)

Heat Evolution and Analysis of Elements for Solid StateElectrolyte in DeuteriumAtmosphere During Applied Electric field

Tadahiko Mizuno, Tadashi Akomoto, Kazuhisa Azumi,
Masatoshi Kitaichi,Kazuya Kurokawa and Michio Enyo.

J. New Energy, **1**, No.1, 79-87(1996)

A proton conductor, the solid state electrolyte, made from oxide of strontium, cerium, niobium and yttrium can be charged in a hot D_2 gas atmosphere to produce excess heat. Anomalous heat evolution was observed for 12 in 80 cases of the samples charged by alternating current for 5 to 45 Volts at temperatures ranging from 400 to 700 C. Several kinds of alkali metals, including Ca, Mg, Bismuth, lantanides and Aluminum were locally segregated and distributed around the melted and swelled parts of the samples that generated an excess heat.

The alleged Cold Fusion reaction still has not confirmed because of lack of data. It is very important to obtain precision relationships quantitatively between each reaction products that may cause from the reaction. We understand that the most desirable parameter to analyze the reaction mechanism is to obtain simultaneously quantities such as heat evolution, neutron emission, tritium generation, and so on. However, this is very difficult due to difficulties to reproduce and control the phenomena. Even if it has been possible, usually the amounts of reaction products are very low and sometimes near or below the detection limit; it is difficult to calibrate quantitatively. Therefore, it is suitable to analyze the element in the sample before and after the experiment. (English)

Anomalous Heat Evolution From a Solid-State Electrolyte under Alternating Current in High-Temperature D2 Gas

Tadahiko Mizuno, Tadashi Akomoto, Kazuhisa Azumi,
Masatoshi Kitaichi, Kazuya Kurokawa and Michio Enyo.

Fusion Technology, **29**, No.3, 385-389(1996)

A coin-shaped proton conductor made from metal oxides of strontium and cerium can be charged in a hot D2 gas atmosphere to produce excess heat. In this study, anomalous heat evolution was observed from the proton conductors charged with alternating current at 5 to 45 Volts, at temperatures ranging from 400 to 700 C. The anomalous heat produced temperature rises as high as 50 C. Excess heat was estimated as a few watts in most cases, totaling up to several kilojoules. The cold fusion reaction can be sometimes identified by a very level of neutron emission, or occasionally by a high level of tritium production. But in most cases, the reaction produces some level of excess heat, and this is the most readily observed signature of the reaction. Reproducibility is generally still poor. The reaction cannot be controlled because the mechanism is not understood. The proton conductors are used in this work as a gas phase electrochemical system, in contrast to the liquid electrochemical systems that are widely used to study the reaction, usually employing heavy water and Pd electrodes. One of the principal experimental difficulties with the liquid phase systems is that it takes an extremely long time to load the deuterium into the metal. On the proton conductor, the reaction begins relatively quickly, usually within a half-hour after the experiment has started. The heat and the reaction products were extremely difficult to reproduce and showed no controllability. These examples suggest that some kind of triggering mechanism may be helpful in this reaction. We assumed that the reaction might occur when a chaotic state is caused by the movement of protons in the lattice. We have therefore used proton conductor ceramics at various temperatures and applied alternating electric fields as a trigger to cause the reaction. These difficulties are often linked with absorption and

diffusion of hydrogen and deuterium; temperature changes introduced by electrolysis; and other factors. Cold fusion reactions are expected to be transitory and unstable under these circumstances; they begin and end spontaneously after long loading periods. We have attempted to get around from these problems and control the reaction by charging at a high temperature in D2 gas. We discovered materials that load in a stable fashion, generating relatively stable, long-lasting reactions. (English)

Anomalous Isotopic Distribution inPalladium Cathode after Electrolysis

Tadahiko Mizuno, Tadayoshi Ohmori and Michio Enyo

Infinite Energy, **2**, No.7 10-14(1996)

Nuclear reactions in a solid electrode at ordinary temperatures have been reported by many experimenters since 1989. However, this phenomenon is still not well accepted among researchers because of poor reproducibility and control. What is urgently needed now is to obtain precise and quantitative relationships between potential nuclear reactions and their corresponding reaction products. If nuclear reactions induced by electrochemical reaction occur in solid electrodes, there must be clear evidence such as the evolution of radioisotopes and radiation. Moreover, the evolution of the reaction products should be explained in terms of the nuclear mechanisms. In this work, evidence which indicates the occurrence of some nuclear reactions is presented, in the form of transmuted elements within the cathode and on the cathode surface. The anomalous isotopic distribution of these elements shows they do not come from contamination. For example, natural copper is 70% Cu63, and 30% Cu65. But the copper found in the cathode was 100% Cu63, with no detectable levels of Cu65. Natural isotopic distribution varies by less than 0.001% for copper.(English)

The Evaluation of Pitting Corrosion from the Spectrum Slope of Noise Fluctuation on Ironand 304 Stainless Steel Electrodes

Toshihiro Fukuda and Tadahiko Mizuno

Corrosion Science, **38**, No.7, 1085-1091 (1996)

Pitting initiation and growth behavior was observed by spectrum analysis method of anodic current fluctuation for pure iron or stainless steel using the low noise potentiostatic condition. This method was found to be useful for prediction of pit generation. The corrosion resistance of iron and stainless steel is taken to be due to formation of a passive film formed on the metal surface. It is possible to estimate a corrosion tendency, as a whole, by various factors, such as the amount of impurity in iron, the composition of the stainless steel, the pH of the solution, the temperature, and the halide ion composition in solution. However, under less corrosive conditions, it is difficult to predict pitting corrosion by these factors. Here, pits are seldom generated but occasionally trigger serious corrosion. The prediction of pitting corrosion at the early stage of corrosion formation is needed for many practical applications. As one of electrochemical methods for pit generation prediction, the power spectrum analysis of electrode potential or current fluctuation has been carried out to give information about apparently random processes of breakdown and reformation of passive films.

In this study, we examined the relation between power spectra and stability of the passive film, and showed the way to predict pitting corrosion generation is by spectrum analysis of current fluctuations of pure iron and 304 stainless steel in a borate buffer solution of pH8.5.(English)

Anomalous Isotopic Distribution of Elements Deposited on Palladium Induced by Cathodic Electrolysis

Tadahiko Mizuno, Tadayoshi Ohmori, Kazuya Kurokawa,
Tdashi Akimoto, Masatoshi Kitaichi, Koichi Inoda,
Kazuhisa Azumi, Shigezo Shimokawa and Michio Enyo

Denki Kagaku, **64**, No.11, 1160-1165 (1996)

It was confirmed by several analytic methods that reaction products with atomic numbers ranging from 20 to 28, 46 to 54, and 72 to 82 are detected in palladium cathodes subjected to elctrolysis in a heavy water solution at high pressure, high temperature and by high current density for one month. Isotopic distributions were radically different from the natural ones.

The elements were changed by metal and electrolysis conditions. These masses were composed of many elements ranged from hydrogen to lead. Extraordinary observations were the changes of their isotopic distributions in the produced elements; these were radically different from the natural ones on the Pd electrode. For example, natural chromium is 4.3% Cr50, 84% Cr52, 9.5% Cr53 and 2.4% Cr54. But the Chromium found on the Pd surface was 14% Cr50, 51% Cr52, 2.4% Cr53 and 11% Cr54. Natural Isotopic distribution varies by less than 0.003% for Cr. Essentially the same phenomenon was confirmed more than ten times with high reproducibility at high cathodic current density, above 0.2 A/cm^2. All the possibilities of contamination had been carefully eliminated by several pretreatment for the sample and electrolysis system. This means that a nuclear reaction had taken place during the electrochemical treatment. This suggests the possible existence of new interactions discovered in the framework of a generalization of the usual quantum mechanics. Thus such new interactions, due to the mutual overlap of wavepackets, may explain the new phenomena experimentally observed in this study.(Japanese)

Isotopic Changes of the Reaction Products Induced by Cathodic Electrolysis in Pd

Tadahiko Mizuno, Tadayoshi Ohmori and Michio Enyo

J. New Energy, **1**, No.3, 31 (1996)

Many elements on Pd electrode were confirmed by several analytic methods; reaction products with mass number up to 208 are deposited on palladium cathodes subjected to electrolysis in a heavy water solution at high pressure, temperature, and current density for one month. These masses were composed with many elements ranged from hydrogen and lead. Extraordinary observations were the changes of their isotopic distributions for the produced elements; these were radically different from the natural ones. It means that a nuclear reaction had taken during the electrochemical treatment. It is discussing the role of new interactions discovered in the framework of a generalization of the usual quantum mechanics. It is evidence that such new interactions, due to the mutual overlap of wavepackets, explain the new phenomenologies that are experimentally observed in this study.

It might be argued that if nuclear reactions have been induced by electrochemical reaction occurring in solid electrodes, there must be clear evidence such as the evolution of radioisotopes and radiation. Moreover, the evolution rates of the reaction products should be quantitatively explained in terms of the proper nuclear reaction mechanisms. Such logic could be applied if the reaction mechanism consists of established mechanisms. However, there is no a priori reason to assume that conventional mechanisms are involved. Thus, the existence of expected radiation signatures can not be assured. In this work, evidence which indicates the occurrence of some nuclear reactions is presented, such as the isotopic variation of elements appearing in and near the cathode surface. These elements appeared without the presence of detectable radiation. The anomalous isotopic distribution of these elements is strong evidence they do not come from contamination. We suppose that the reaction mechanism may be completely different from known nuclei formation processes. However, we attempt to explain the process which produced these anomalous products theoretically. (English)

Modeling of Ion Exchange Reactions on Metal Oxides with the Frumkin Isotherm
1 .Acid-Base and Charge Characteristics of MnO_2, TiO_2, Fe_3O_4, and Al_2O_3 Surfaces and Adsorption Affinity of Alkali Metal Ions

Hiroki Tamura, Noriaki Katayama, and Ryusaburo Furuichi

Environmental Science and Technology,
30, 1198-1204 (1996)

Metal oxides abundant in natural environments affect the concentrations of ions in waters by adsorption. The ion adsorption ability of oxides arises from the acid-base nature of surface hydroxyl groups formed by dissociative chemisorption of water molecules. The protonation and deprotonation reactions of hydroxyl groups produce electric charges, resulting in ion adsorption to maintain electric neutrality (ion exchange). The amount of surface charge in alkali metal nitrate solutions was measured as a function of pH by titration, and the ion-exchange reactions accompanying the charge formation were modeled by using the Frumkin isotherm, which assumes suppression of the reaction due to lateral interactions between the interphase species. This model embodies not only electrical, but also chemical, geometrical, and/or other lateral interactions and can be applied to "real", not well defined oxide/solution systems in natural environments. From the model parameters, it was found that the intensity of cation exchange (acid dissociation) increases in the order: $Al_2O_3 < Fe_3O_4 < TiO_2 < MnO_2$, and the intensity of anion exchange (base dissociation) decreases in the same order. The electronegativity of the lattice metal ions of these oxides was estimated and found to increase in the order above. It is suggested that, with electronegativity of the lattice metal ions, the electron density of adjacent lattice oxide ions and hence the acid-base nature of hydroxyl sites changes. Also, the adsorption affinity of alkali metal ions was evaluated and discussed with the model parameters. (English)

Effect of Dissolved Oxygen on the Dissolution Rate of Magnetite in EDTA Solutions

Shinichi Takasaki, Kazuyoshi Ogura,
Hiroki Tamura, and Masaichi Nagayama

Zairyo-to-Kankyo (Corrosion Engineering), **45**, 67-74 (1996)

The dissolution rate of sintered Fe_3O_4 pellets in 3 mod/m^3 EDTA (H_4Y) solutions with and without dissolved oxygen (DO) was measured at different pHs (1.1 ~ 4.6) at 80℃. The dissolved Fe concentration increases with time in a parabolic manner, exceeding the EDTA concentration in the absence of DO but not exceeding the EDTA concentration in the presence of DO. The rate of dissolution changes with pH, with and without DO. The dissolved Fe concentration vs. pH curves for different dissolution times show maxima at pH 2.4, and the rates without DO are always higher than those with DO. It is assumed that the dissolution reaction involves two coupled processes: (a) the transfer of Fe ions by reaction with EDTA to form $Fe^{III}Y^-$ and $Fe^{II}Y^{2-}$; and (b) the transfer of lattice O^{2-} ions by reaction with H^+ ions to form H_2O. In the absence of DO, the formed $Fe^{II}Y^{2-}$ reacts with Fe^{3+} to dissolve further Fe_3O_4, and can be regarded as equal to free EDTA. The rate equation explaining the dissolution without DO is derived as follows:

$$\frac{d[\mathrm{Fe}]}{dt} = \frac{k'k''[H^+]^{8/3}\alpha([Y]_T-2[\mathrm{Fe}]/3)}{(2^{2/3}/3)k'[\mathrm{Fe}]+k''[H^+]^{8/3}} \tag{1}$$

where [Fe] = $[Fe^{II}Y^{2-}]+[Fe^{III}Y^-]$, k' and k" are composite rate constants, a is the fraction of Y^{4-} in free EDTA, and $[Y]_T$ is the total concentration of added EDTA. In the presence of DO, the formed $Fe^{II}Y^{2-}$ is instantly oxidized to $Fe^{III}Y^-$, and the rate equation for this condition was reported elsewhere. The rate equation for conditions with and without DO reproduce the time-courses of [Fe] well, and the calculated [Fe] vs. pH curves show peaks at pH 2.4. The rate constants k' and k" are not affected by DO, and the effect of DO on the dissolution rate is due to different "effective" EDTA concentations: with DO, the dissolved Fe is $Fe^{III}Y^-$, which does not take part in further dissolution, without DO, one third of the dissolved Fe is $Fe^{II}Y^{2-}$, this can dissolve further Fe_3O_4 to form $Fe^{III}Y^-$ and Fe^{2+}. (Japanese)