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The our research activity is concerned with corrosion and corrosion protection of metals, development of recovery system of aluminum scrap, and artificial model for photosynthesis.

Research programs in progress are as follows:

Current Activities and Presentations

(1) Semiconductive properties of passive films

The protective oxide films on metals are one of important factors for understanding the corrosion phenomena of metals. The semiconductive properties of the oxide films were examined by measurement of electronic current from redox species in the aqueous solution on passivated iron and stainless steels. The interfacial properties on the passivation oxide-covered electrodes were also estimated by AC impedance and AC potential modulation reflectance. The iron passive films behaves as an n-type semiconductive electrode, where the electronic flow from Fe^{3+}/Fe^{2+} redox in the solution is suppressed by a depletion layer in the potential region more positive than the flat-band potential. This rectification effect is also observed on the passive film of stainless steels, however no suppression is observed on the passive films of nickel. Further examination of the nickel passiveation film will be required and the ellipsometric and AC technique measurement is under investigation.

(2) Artificial model for photosynthesis

In the bioreaction, the quinone and porphyrin derivatives play a large role in electron and /or proton transfer for energy production. In the bacterial photosynthesis, the electron excited in chlorophyl transfers quinone derivatives with high efficiency. Electrode systems modified by quinone derivatives were constructed for achievement of highly efficient electron transfer. The phospholopid linked with metal porphyrin was casted on a glassy carbon electrode and the redox behavior of the porphyrin in the modified electrode was studied in an aqueous solution. The redox current was observed which depends on the temperature and the spacer length between the porophyrine and phospholopid. We synthesized the naphthoquinone-bond dialkyl disulfides with different lengths of spacer alkyl chain and form self-assembled monolayers on a gold electrode. On the voltammogram a clear redox wave was observed. AC potential modulation reflectance was applied for insight of the transfer mechanism. The reflectance change was observed at the potential at which the redox reaction of the monolayer takes place. From the comparison with differential capacitance, the mechanism of the electron transfer was discussed.

(3) Surface layers on metals in gaseous corrosion environments

Surface layers initially formed on copper in gaseous corrosion environments were investigated by in situ IR-RAS and QCM techniques. The corrosion test was carried out in air with the concentration ranges of 60-90% RH(relative humidity) for water vapor and 1-20 ppm for SO_2 gas. On the basis of 2D-IR analysis of IR-RAS spectra, the components of the layer of corroded surfaces were elucidated as Chevreul's salt ($CuSO_3 \cdot Cu_2SO_3 \cdot 2H_2O$),$CuSO_4 \cdot 5H_2O$, and water layer. The time variations in their quantities were also determined by combined analysis of time-resolved IR-RAS spectra and mass gains from QCM measurements. The effects of concentrations of water vapor and SO_2 on the formation rates of them were also investigated.

(4) Corrosion of materials for lead free solder

Corrosion of binary tin alloys (Sn-Zn, Sn-Bi and Sn-Ag) at the eutectic compositions were investigated in sulfuric and nitric acids. The quantities of dissolved components of the alloys were determined together with surface analysis of the samples. In both acids, the Sn component preferentially dissolved from the Sn rich solid solution phases of Sn-Bi and Sn-Ag alloys, and both Zn and Sn components dissolved from Sn-Zn alloy, but the dissolution rates were higher in nitric acid than in sulfuric acid. Sn was easily passivated in weak acid solutions and no dissolution of all metal components except Zn was admitted, whereas the lead component in lead eutectic solder was significantly dissolved.

(5) Adsorption of thiourea on gold electrode

Adsorption behavior of thiourea on a gold electrode was investigated in perchloric acid by in situ IR-RAS and QCM. The gold electrode contacted with perchloric acid solution of thiourea was covered with thiourea molecules through specific adsorption and hydrogen evolution reaction is inhibited. By potential shift to positive region, one electron oxidation of thiourea occurred and resulted in formation of a mercaptid bond.

(6)Development of corrosion inhibitors

The inhibition mechanisms of newly-developed corrosion inhibitors for steels, copper and aluminum have been studied using electrochemical AC impedance spectroscopy and surface-enhanced Raman spectroscopy.

(7)Copper tube corrosion and its protection

Localized "ant's nest " corrosion in copper tubes for heat-transfer units has been investigated. Protectiveness of different types of coatings on copper tube surfaces are being evaluated after exposure to simulated corrosive environments.

(8)Recovery of aluminum from aluminum dross

Recovery of metallic aluminum from aluminum dross comprised of Al alloy, Al oxides, and other metal oxides were examined. The metallic aluminum was completely separated from the oxide components by floating of liquid metallic aluminum in a chloride-fluoride mixture molten salt.

(9)Formation of corrosion resistance film by molten salt electrolysis

To improve the corrosion resistance of TiAl inter-metallic compound in high temperature, we have developed with molten salt electrolysis a new coating layer consisting of Al-Cr alloy. The Al-Cr alloy was deposited on TiAl cathode in molten salt mixture of aluminum chloride, sodium chloride, and potassium chloride containing chromium chloride at 150°C. The composition of Al-Cr alloy was found to depend on potential during electrolysis.

Other Activities

The following foreign scientist visited this laboratory: Dr.Kyung-Suk Yun, Korea Institute of Science and Technology, Korea on May 24-26.

Prof. Ohtsuka attended ‘99 Asian Conference on Electrochemistry, Tokyo, Japan, May 19-21, 1999 and presented a paper entitled by photo-induced change of anodic oxide films on titanium by ellipsometry and AC Impedance. Dr. Notoya had a special lecture on "Copper and Life" at Akita University in July. He received the Japan Copper Center Awards for the excellent achievements in the elucidation of the mechanisms of copper and its alloys corrosion and the development of anti-corrosion technology in May.Prof. Ohtsuka, Dr. Notoya, and Dr. Ueda attended the 1999 Joint International meeting of ECS and ECS Jpn, Honolulu, Hawaii, USA, Oct.17-22 (1999) and presented four papers entitled by Potential modulation reflectance of passivated iron and nickel, UV light induced change of anodic oxide films on titanium in acidic Sulfate solution, localized "ant's nest" corrosion in copper tubes caused by aldehyde and ketone, and cell efficiency on bipolar electrode cell for aluminum electrorefining. Dr. Notoya participated in Corrosion & Prevention 99 conference, Sydney, Australia, Nov. 21-24 (1999).

Presentations

Cell Efficiency of a Bipolar Electrode System for Aluminum Electrorefining; M. Ohmura, M. Ueda, S. Konda, T. Sasaki, and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf, Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Sapporo, Jan., 1999.

Potential modulation Reflectance of a Gold Electrode Modified by SAMs Containing Naphthoquinone; T. Ohtsuka, H. Komori, M. Nagata, M. Nango, ibid.

Influence of Surface Preparation in Initial Stage of Copper Corrosion; J. Ito, T. Sasaki, and T. Ohtsuka, ibid.

Effect of Surface States on Initial Corrosion behavior of Copper in Humid Air Containing Sulfur Dioxide; J. Itoh, T. Sasaki and T. Ohtsuka: ibid.

Dissolution Behavior of Al_2O_3 into the Chloride- Fluoride Mixture Molten Salt for Recovery of Aluminum from Aluminum Dross; M. Amemiya, M. Ueda, and T Ohtsuka, ibid.

Corrosion Prevention Effect of Steel Fibers on Steel Bars in Concrete; T.Notoya, A Keyvani Someh and N. Saeki, The Winter Joint Meeting of the Hokkaido Section of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan. 1999

Recent Investigation of Passivation Films on Metals; T. Ohtsuka, The Spring Annual Meeting of Jpn Inst. Met. in 1999, Tokyo, March, 1999.

Inhibition Action of Carboxybenzotriazoleoctylester for Copper Corrosion in Sulfuric Acid;T.Notoya, The 76th Spring Meeting of Japan Chemical Society, Yokohama, March 1999

Change in Properties of Passivation Films on Titanium under uv Light Irradiation by Ellipsometry; T. Ohtsuka and T. Otsuki, The 66th Annual Meeting of Electrochem. Soc. Jpn. , Tokyo, April 1998.

Electrochemical and Optical Investigation of Passivation Films on Metals for Understanding the Resistive Properties; T. Ohtsuka, ibid.

Potential Modulation Reflectance Spectroscopy of of a Gold Electrode Modified by SAMs Containing Naphthoquinone; T. Ohtsuka, H. Komori, M. Nagata, M. Nango, ibid.

Analysis of Operation Characteristics in a Bipolar Cell for Electrorefining of Aluminum; M.Ueda, T.Ohmura, S.Konda, T.Sasaki, T.Ohtsuka, ibid

Examination of Stability Estimation of Iron Rusts; T. Ohtsuka, The 6 th Annual Meeting for "Sabi" Science, Tsukuba, April, 1999.

Application of IR-RAS and 2D-IR to Determination of Corrosion Products Initially Formed on Copper in Air Containing Water Vapor and SO_2; J. Itoh, T. Sasaki, T. Ohtsuka and M. Osawa: The 195th Meeting of ECS, Seattle, May,1999.

In-situ IR-RAS Technique for Investigation of Corrosion layer Initially Formed on Metals in Gaseous Environment; T. Sasaki, J. Ito and T. Ohtsuka, The 8th International Symposium on the Passivity of Metals and Semiconductors, Jasper, Alberta, Canada, May, 1999.

Photo-induced Change of Anodic Oxide Films on Titanium by Ellipsometry and AC Impedance; T. Ohstuka and T. Otsuki, '99 Asian Conference on Electrochemistry, Tokyo, May, 1999.

Effect of SO_2 and Relative Humidity on Corrosion Rate of Copper; J. Itoh, T. Sasaki and T. Ohtsuka: The 1999 Annual Meeting of Jpn Soc. Corros. Eng., Narashino, May, 1999.

In situ Infrared Reflection Absorption Spectroscopy for Investigation of Corrosion Phenomena;ibid.

Capacitance Change of Titanium Anodic Oxide Film by uv Light Irradiation; T. Ohtsuka and T. Otsuki, ibid.

Aluminum Electrorefining from Aluminum Alloy Containing Magnesium; S. Tsukamoto, M Ueda, S. Konda, and T. Ohtsuka, The 1999 Joint Meeting of Hokkaido Sections of JIM and ISIJ, Muroran, July, 1999.

Protection of Zinc with Conductive Polyaniline; S. Mucha, M. Ueda, S. Konda, and T. Ohtsuka, ibid.

Electrochemistry of Corrosion Products; T. Ohtsuka, The 3rd Workshop on Corrosion and Protection of Zn-prepared Surface Finishing, Kawasaki, July, 1999.

Environmental Corrosion Factors on the Localized Corrosion of Copper Tubes in

Air-conditioning Units.T. Notoya, T. Ohtsuka, T. Atsumi, K.Kawano, T. Ando and M.Niwa, 1999 Summer Hokkaido Branch Meeting of Japan Chemical Society, Tomakomai, July, 1999.

Potential Modulation Reflectance of Passivation Film on 304 and 316 Stainless Steels; M. Komoto and T. Ohtsuka, The 46th Discussion Meeting of Jpn Soc. Corros. Eng., Fukuoka, Sept., 1999.

Reaction rate of Fe(II)/Fe(III) Redox and Semiconductive Properties of Passivation Films on Iron; R. Ozaki and T. Ohtsuka, ibid.

Corrosion Behavior of Lead Free Solders in Sulfuric Acid Solution; M. Mori, T. Sasaki, K. Miura, and T. Ohtsuka, ibid.

Adsorption of Thiourea on a Gold Electrode in Perchloric Acid Solution, N. Yuuki, T. Sasaki, and T. Ohtsuka, ibid.

Corrosion Behavior of Copper in Wet Air Containing SO_2, J. Ito, T. Sasaki, and T. Ohtsuka, ibid.

Electron Transfer of Quinone Derivatives in a Modified Electrode; M. Nagata, Y. Suemori, T. Ohtsuka and M. Nango, The 14th Symp. on Biofunctional Chemistry, Sapporo, Sept., 1999.

Redox Reaction of Iron Electrode Covered with Passivation Thin Film; R. Ozaki and T. Ohtsuka, The 77th Autum Annual Meeting of Jpn Chem. Soc., Sapporo, Sept., 1999.

Role of Steel Fibers in the Corrosion Protection of Steel Bars in Concrete; T. Notoya, T. Ohtsuka, T. Saeki and Keyvani Someh, The 77th Fall Meeting of Japan Chemical Society, Sapporo, Sept. 1999.

Recovery of aluminum alloy from aluminum dross by chloride-fluoride mixture melt; M.Ueda, M. Amemiya, and T .Ohtsuka, The 100th Annual Meeting of Sur. Finish. Soc. Jpn.,Nagoya, Oct.,1999.

Potential Modulation Reflectance of Passivated Iron and Nickel; T. Ohtsuka, The 1999 Joint International meeting of ECS and ECS Jpn, Honolulu, Hawaii, USA, Oct., 1999.

UV Light Induced Change of Anodic Oxide Films on Titanium in Acidic Sulfate

Solution; T. Ohtsuka and T. Otsuki, ibid.

Localized "Ant's Nest" Corrosion in Copper Tubes Caused by Aldehyde and Ketone; T. Notoya, T. Ohtsuka, T. Atsumi, K. Kawano, T. Ando, and M. Niwa, ibid.

Cell Efficiency on Bipolar Electrode Cell for Aluminum Electrorefining; M. Ueda, T. Ohmura, S. Konda, T. Sasaki, and T. Ohtsuka, ibid.

Effect of Oxide Layers on Initial Corrosion of Copper; J. Itoh, T. Sasaki and T. Ohtsuka: Research Meeting on Materials and Environment for the 21st Century, Institute for Materials Research, Sendai, Nov. 1999.

Operation Characteristics in a Bipolar Cell in Electrorefining of Aluminum; M. Ueda,, S. Konda, T. Sasaki, T. Ohtsukai, ibid.

Localized Corrosion in Copper Tubes by Volatile Substances from Woods;T. Notoya, T. Atsumi, M. Niwa, K. Kawano and T. Ando, The 46th Conference of Materials and Environments, Fukuoka, Nov. 1999.

Elucidation of Initial Stage of Corrosion of Copper in Gaseous Environment by IR-RAS; J. Itoh, T. Sasaki and T. Ohtsuka: Discussion Meeting on Photochemistry on Solid and Surface, Sapporo, Nov. 1999.

Corrosion Inhibition of Copper with Carboxybenzotriazolealkylesters; T. Notoya, T. Ohtsuka, Bing Wang, Guo-ding Zhou and Wan-You Zhang, The Summer Meeting of Hokkaido Section of Japan Institute of Metals,Muroran, Nov. 1999

CopperCorrosion Inhibition by Carboxybenzotriazolealkylesters; T. Notoya, D.P. Schweinsberg, S.E. Bottle and N. Huynh, The 39th Meeting of Japan Copper and Brass Research Association, Kyoto, Nov. 1999.

Effect of Formic Acid on the Formation of Copper Oxides in Wet Atmospheres
M. Miyazaki, T. Ohtsuka and T. Notoya, ibid, Kyoto, Nov. 1999

Inhibition of Copper Corrosion with Esters of 4- and 5-Carboxybenzotriazole
N. Hnynh, S.E. Bottle, T. Notoya and D.P. Schweinsberg

Corrosion & Prevention 99, Sydney, Australia, Nov. 1999.

Investigation of Initial Step of Corrosion in Gaseous Environment by in situ
IR- RAS; J. Itoh, T. Sasaki and T. Ohtsuka: The 18th Meeting on Spectroscopy of Adsorbed Molecules, Otaru, Dec. 1999.

Analysis of Iron Rust layer by Various Instruments; T. Ohtsuka, The 123rd Symp. on Corrosion and Corroson Protection of Jpn Soc. Corros. Eng., Tokyo, Dec., 1999.

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Our research activities are in developing materials with functions of corrosion resistance, separation, photo-electrochemical conversion, and others, where the methods of characterization and evaluation of the properties of the materials, in relation to surface reactions, surface compositions, and surface morphologies, are also being developed.

The research programs in our laboratory are:

(1) Preparation and characterization of γ-FeOOH

Iron oxyhydroxide γ-FeOOH is a compound found in the rust layers of well functioning steels resistant to weathering. Here, γ-FeOOH was prepared by oxygenation of Fe(II) salt solutions with different pH and concentrations to establish conditions under which this oxyhydroxide is formed. The product γ-FeOOH was examined by thermal analysis, XRD, and BET specific surface area measurements. It was found that γ-FeOOH formed in the pH region 6-8, and that the crystallite size was the largest at pH 7 and the specific surface area the smallest at pH7.5. The crystallite size increased with increasing Fe(II) concentration and aging time.

(2) Adsorption of sodium ions on surface hydroxyl sites on spinel type manganese oxide

A spinel type manganese oxide ($\square Mn_2O_4$) with vacancies (□) is a "lithium ion memory" template ion exchanger, and has shown promise for the recovery of lithium from sea water and for preliminary concentration of trace lithium in natural environments. This oxide has surface hydroxyl groups like other metal oxides, and non-specific ion-exchange reactions at hydroxyl sites also takes place. The amount of sodium ions adsorbed was measured as a function of pH and modeled to assess contamination.

(3) Determination of surface hydroxyl site density of metal oxides

Metal oxides have ion-exchange properties due to surface hydroxyl groups formed by dissociative chemisorption of water molecules. The surface hydroxyl site density of metal oxide samples was measured by the Grignard reagent method as a measure for the ion-exchange capacity. The results were about the same, comparable to the value attained by the closest packing of hydroxide ions. A new mechanism of hydroxylation was proposed, where the surface lattice oxide ions (not lattice metal ions) are hydrated.

(4) Dissolution of metal oxides in chelating agent solutions

The structural components of cooling systems of (nuclear) power plants are covered with metal oxides 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 CuO, PbO, Fe_2O_3 in EDTA solutions was measured as a function of pH and EDTA concentration. The dissolved ion concentration showed a peak at specific pH. Our mechanism proposed for magnetite was able to apply to these oxides, where lattice metal ion transfer by chelation with EDTA is combined with lattice oxide ion transfer by protonation to keep electric neutrality.

(5) REM effect on high temperature oxidation of Fe-Cr alloys

The favorable effect of REM on high temperature oxidation of chromia forming alloys is well known but no explanation of the effect is established. In this study, oxidation of Fe-16Cr alloys with lanthanum hydroxide coatings was carried out at 1373 K. It was found that the growth rate and the time to rupture of the scales are improved with 10^{16} atom cm^{-2} of coating. The value is similar to a reported one at which the growth of oxide scales changes from predominantly cationic to anionic transport. Iron rich oxide particles formed initially and converted to a chromium rich layer. This cannot be explained by the nucleation model, and the change in growth mode of oxide scale seems to be the reason for the REM effect.

(6) Initial stage of the high temperature oxidation of low chromium alloys

Thin oxide scales initially forming on most heat resistant alloys sustain the corrosion resistance. However, the critical content of chromium to form chromium-rich scales on chromia forming alloys is not clear. In this study high temperature oxidation of Fe-Cr binary alloys containing 5 to 18 mass% was carried out at 1173 K for several seconds upto 5 minutes. Analysis of the oxide properties showed that the crytical content is 11 mass%. This value coincides with the transition from α to γ phase of the underlying alloys. It is suggested that the formation of chromium-rich scales is related to lattice diffusion of metallic species in the alloys.

(7) Oxide film formation at high temperature under constant stress

Thin oxide scales formed on Fe-16Cr alloy have been found to contain equal amounts of iron and chromium in past studies. Simultaneous ionization of iron and chromium at oxide/alloy interfaces is difficult to explain if outward migration of cations is predominant in the scale growth. It has been proposed that mechanical breakage due to growth stresses and restoration of the scales may occur during the growth caused by the formation of iron containing scales. To verify this mechanism, high temperature oxidation study of Fe-Cr alloys under tensile stress, which may counteract the growth stresses, is planned. Apparatus for the study has been installed and the work is now in progress.

(8) Preventing photo-electrochemical corrosion of zinc oxide

Zinc oxide has the potentials to oxidize substances in aquatic media at negative potentials under UV light because of its positive valence band level. However, photo-electrochemical corrosion of ZnO itself occurs in such a situation. Stable titanium oxide is added to ZnO and photo-electrochemical corrosion tests were carried out for several days. It was shown that the corrosion takes place in the early stage of the test and then stops, even when a high anodic current due to oxygen evolution reaction is maintained. A thin titanium oxide layer on the ZnO surface prevents the corrosion and protects the underlying ZnO to sustain the high anodic current.

Presentations

Effect of La Hydroxide Coatings on the Oxide Composition and Structure Formed on SUS430 Stainless Steel at 1373 K; A. Saito, I. Saeki, and R. Furuichi: The 1999 Joint Meeting of Hokkaido Sec. Of Electrochem. Soc. Jpn, Surf. Finish. Soc. Jpn, and Jpn. Corros. Eng. Soc., Sapporo, Jan., 1999.

Determination of Surface Hydroxyl Groups on Metal Oxides as the Sites for Ion-Exchange, Their Origin and Reactivity ; H. Tamura and R. Furuichi: The 1999 Winter Joint Meeting of the Hokkaido Secs. of Jpn. Soc. for Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1999.

Properties of the Oxide Films Formed on SUS430 Stainless Steel Coated with La Compound Oxidized at Elevated Temperatures; A. Saito, I. Saeki, and R. Furuichi: The 137th Annual Meeting of Iron and Steel Institute of Japan, Tokyo, Mar., 1999.

Density, Ion-Exchange Property, and Formation Mechanism of Surface Hydroxyl Groups on Metal Oxides; H. Tamura and R. Furuichi: The 76th Spring Annual Meeting of Chem. Soc. Jpn., Tokyo, Mar., 1999.

Effect of Cr on the Properties of Oxide Films formed on Fe-Cr Alloys Oxidized at 1173 K; H. Takeda, I. Saeki, and R. Furuichi: The 1999 Annual Meeting of Jpn. Soc. Corros. Eng., Tokyo, May,1999.

Colloid Chemistry of Corrosion Products -Hydroxylation, Ion-Exchange Reaction, and Surface Charge Formation on Metal Oxide Surfaces-; H. Tamura: The 3rd Seminar of the Steel Forum, Soga, Chiba, July, 1999.

Thoughts on Environments,Recycling, and Surface Technology; R. Furuichi: The 1999 Summer Seminar, Sapporo, Aug, 1999.

High Temperature Oxidation of Lanthanum Coated Type430 Stainless Steel; I. Saeki, A. Saito, and R. Furuichi: 14th international Corrosion Congress, Cape Town, 1999.

High Temperature Oxidation of Fe-5~18Cr Alloys in Air; H. Takeda, I. Saeki, and R. Furuichi: The 125th Annual Meeting of Jpn. Inst. Metals: Kanazawa, 1999.

Thermal Analysis of the Rusts Formed on Weathering Steels; H. Tamura: Rust Science Society, Tokyo, Nov., 1999.

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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, hydrogen adsorption / absorption, and surface finishing.

Current topics on research are as follows :

(1) Measurement of stresses generated during anodic oxidation of titanium thin films by a laser beam deflection method

The stress changes of titanium film during anodic oxidation in pH 8.4 borate, pH 6.9 phosphate, 0.1 M HCl and 0.1 M H_2SO_4 solutions were measured as a function of anodic potential by a laser-beam deflection method. The compressive stress accumulated in the anodic oxide film on titanium increased with increasing the anodic potential, depending on the electrolyte solutions. The derivative of the compressive stress with electrode potential, however, took a maximum at about 8 V_{RHE}, irrespective of the electrolyte solutions. At the potential higher than 8 V_{RHE}, the cracks in the oxide film were observed with an atomic force microscope (AFM). The rapid decrease in the derivative of the compressive stress with electrode potential at the potential higher than 8 V_{RHE} may be ascribed to the release of stress due to the crack formation in the film. Moreover, the component of compressive stress due to the electrostriction in anodic oxide film on Ti was measured by a cathodic potential sweep from the film formation potential to 0 V_{RHE} corresponding to a flat band potential of TiO_2 film at which no electric fields are present in the film. The measured component of compressive stress due to the electrostriction was 1.5×10^7 N m^{-2} which was the same order of the magnitude as that calculated but was only 2 % of the total compressive stress due to the film formation.

(2) Mechanical properties of the titanium thin films anodically oxidized

Titanium thin films with thickness of 250 nm were deposited on glass plates with a magnetron sputtering method. Nanoindentation tests were performed to evaluate the mechanical properties of the titanium film surfaces anodically oxidized at different potentials for 1 h in 0.1 M HCl, 0.1 M H_2SO_4 , pH 8.4 borate and pH 6.9 phosphate solutions. The hardness and elastic modulus of the titanium thin film surfaces anodically oxidized in 0.1 M H_2SO_4 were larger than those in other three different solutions. The compressive stresses generated in anodic oxide films during anodic oxidation of titanium thin films in 0.1 M H_2SO_4 were also larger than those in other three different solutions, suggesting the correlation between mechanical properties and stresses in anodic oxide films. Both the hardness and elastic modulus of titanium thin film surfaces decreased at the potential higher than 5.7 V (RHE), irrespective of kinds of electrolyte solutions used, which were ascribed to the release of compressive stress due to the partial breakdown of anodic oxide film.

(3) Piezoelectric detection of changes in surface energy of platinum electrode in alkaline solutions

The changes in surface energy of platinum electrode in alkaline solutions of pH 9 - pH 13 containing 0.5 M NaF as supporting electrolyte were detected by a piezoelectric response method to understand the specific adsorption of OH^- ions and the structural changes of electric double layer. The potential of electrocapillary maximum (pem) or potential of zero charge (pzc) of platinum electrode could be measured as a function of solution pH. Moreover, the characteristic potential, E_{max}, at whcih the amplitude of the piezoelectric signals took maximum, emerged in the potential range between pem or pzc and the potential of PtO monolayer formation. The pH dependence of E_{max} was - 0.06 V / pH which was the same as the pH dependence of pem or pzc. It was suggested that the specially adsorbed OH^- ions would form PtOH at E_{max} accompanying the charge transfer and inducing the strucutural changes of electric double layer.

(4) EQCM analysis of mutual conversion processes of $Ni(OH)_2$ and NiOOH

Mutual conversion processes of $Ni(OH)_2$ and NiOOH in KOH or NaOH solution were investigated with EQCM. $Ni(OH)_2$ film was electrochemically deposited on a gold electrode of AT-cut, 5 MHz quartz oscillator by a cathodic polarization under a galvanostatic condition in 0.1 M $Ni(NO_3)_2$ solution. It was found that the mutual conversion proceeded with about 100 % current efficiency in 0.1 M KOH or 0.1 M NaOH. Moreover, it was estimated that during the conversion process from $Ni(OH)_2$ to NiOOH, K^+ of 0.12 mol per $Ni(OH)_2$ of 1 mol was incorpolated for 0.1 M KOH, whereas Na^+ of 0.18 mol was incorpolated for 0.1 M NaOH.

(5) Cathodic decomposition of InP in HCl

The cathodic decomposition (corrosion) of n-type InP in 1.0 M HCl was investigated under cathodic polarization in the potential region of - 0.7 V (SHE) to - 1.1 V (SHE) for a certain period and followed by anodic potential sweep. After the cathodic polarization, the anodic current peak was observed at - 0.47 V (SHE) during the anodic potential sweep. The anodic current peak was ascribed to the anodic dissolution of In which was deposited on InP surface due to the cathodic decomposition ($InP + 3 H^+ + 3 e^- \rightarrow In + PH_3$). The current efficiency of the decomposition reaction taking place in parallel with hydrogen evolution was evaluated from the ratio of the anodic charge for anodic dissolution of deposited In to the total cathodic charge for both cathodic decomposition of InP and hydrogen evoultion. The AFM observation indicated that the surface roughness of InP increased with increasing the cycle of cathodic polarization and anodic potential sweep.

(6) Evaluation of heterogeneity of oxygen evolution on titanium electrode during anodic oxidation by scanning electrochemical microscopy

Probe current images of the anodic oxide film grown on a polycrystalline titanium electrode were measured with two different modes of scanning electrochemical microscope (SECM): a) reduction current of oxygen evoluted in parallel with the growth of anodic oxide film in 0.1 mol dm^{-3} H_2SO_4, and b) oxidation current of $Fe(CN)_6^{4-}$ reduced on anodic oxide film in pH 8.4 borate solution after the film formation for 1 h in 0.1 mol dm^{-3} H_2SO_4. Both probe current images gave the good coincidence, particularly in the point that the anodic oxide film depends on the substrate crystal grain, indicating that the measurement of oxygen reduction current by the probe electrode is useful as an in-situ method for evaluating tha heterogeneity of anodic oxide film formed in the potential region where the oxygen evolution takes place simultaneously.

(7) Development of liquid-phase ion gun for local breakdown of passive film on iron electrode

A silver/silver chloride microelectrode was developed as a liquid phase ion-gun for investigation of precursor process of pitting corrosion. This electrode was set as a probe electrode of a scanning electrochemical microscope (SECM) and used to induce a local breakdown of passive film on iron. A small amount of chloride ions generated by cathodic polarization of the silver/silver chloride microelectrode has succeeded in inducing the local breakdown of the passive film formed on iron in deaerated pH 6.5 borate solution. Moreover, the microelectrode could detect ferric ions dissolved from the film at the initial stage of the film breakdown.

(8) In-situ monitoring of hydrogen evolution from magnetite during galvanic coupling with carbon steel by using a microelectrode

Corrosion of carbon steel in deaerated aquaous solution was accerated by a galvanic coupling with magnetite. In this case, cathodic reaction taking place on magnetite during the coupling with carbon steel should be a) reduction of H_2O, that is, evolution of hydrogen and/or b) reduction of magnetite itself.

Microelectrode was applied to evaluate the amount of hydrogen generated from magnetite during the coupling with carbon steel in 0.1 mol dm^{-3} Na_2SO_4 solution or 0.5 mol dm^{-3} NaCl solution. At a steady state of the coupling in both solutions, about 50 % of cathodic current flowed through magnetite was contributed from hydrogen evolution reaction on magnetite.

(9) Double zincate pretreatment of Al alloy in a LiOH-based zincate solution

A double zincate pretreatment of Al for plating was investigated in a LiOH-based zincate solution. The zinc deposition rate from the LiOH-based zincate solution was lower than that from NaOH or KOH-based solutions, resulting in decreased deposition of Zn and dissolution of the Al substrate. This phenomenon was interpreted as a large coordination number for water molecules to bond with Li^+ ions compared to Na^+ and K^+ in the zincate solutions. For a LiOH-based zincate solution at a concentration near the solubility limit of water, the concentration of free water molecules decreases due to a strong restriction around Li^+ ions. This situation results in a decrease of the activity coefficient of OH^- which leads to dissolution of the Al substrate and decreases the coordination number for water molecules to in relation to $Zn(OH)_4^{2-}$ ions to accelerate the electron transfer from and Zn deposition on the Al substrate. Addition of Fe(III) ions to the LiOH-based zincate solution increased the rate of Zn deposition, suggesting that the co-deposition of Fe obstructs the growth of Zn deposition and results in imperfect insulation of the Al substrate by Zn deposition.

(10) Application of resistmetry on metal dissolution and oxide film formation

Electric resistance of Fe-wire electrode (0.1 mm in diameter) was measured during potential scanning in borate solution at neutral pH. Resistance increased in the range of active potential region, corresponding to decrease in the area of cross section of the iron wire due to active dissolution of Fe. Dissolved thickness was evaluated to be several tenth nm from the resistance change, and that is in good agreement with the value calculated from electric charge of active dissolution. For Al and Ti electrodes resistance was monitored during galvanostatic polarization up to ca. 600 V of cell voltage. In both cases the resistance increased with thickening of the anodic oxide films. The thickness / voltage ratio of the anodic oxide film on Al was calculated to be ca. 1.7 nm V^{-1} which is rather higher than the value previously reported. For the case of Ti, however, the resistance is dependent not only on growth of the oxide film but also on bias voltage and temperature of the specimen. These results indicate that the resistmetry could be an useful in-situ technique for the study of electrochemistry and corrosion research.

(11) In-situ depth profile measurement of plated metals using light emission technique

In the spectra of light emitted from metal electrodes during high voltage cathodic polarization, emission lines corresponds to the atomic elements of electrode material due to formation of plasma phase between electrode surface and solution are observed. Electrode surface is also bombarded by charged particles from the plasma phase, resulting in gradual sputtering of the surface. From these facts an in-situ measurement of the depth profile of atomic elements of electrode surface in the electrolyte solution is expected. Pt and Al wire electrodes with Cu plated layer at various thickness were prepared as model specimen, and the intensity of emission lines were measured as a function of electrolysis time under the glow discharge state. For the case of Pt/Cu electrodes predominant light emission was changed from Cu to Pt during sputtering, depending on the thickness of Cu layer. However, quantitative analysis of composition is, at this time, difficult because of instability in light intensity. For the case of Al/Cu electrode, Cu plating layer was peeled off due to heat generation on the electrode. Further improvement in experimental technique, therefore, is necessary.

Other Activities

From March 26 to April 4, Prof. M. Seo visited Dr. Gyözö. Láng, Department of Physical Chemistry, Eötvös Loránd University, Budapest, Hungary to conduct the research on determination of surface energy of solid electrodes by Hungarian-Japanese Intergovernmental Cooperation and presented the seminar entitled " Application of Scanning Electrochemical Microscope (SECM) to Passive Metal Surfaces".

From April 25 to November 21, Dr. Gyözö. Láng, Department of Physical Chemistry, Eötvös Loránd University, Budapest, Hungary stayed this laboratory as the visiting professor financially supported by the Japan Society for the Promotion of Science (JSPS) and conducted the collaboration research on determination of surface energy of solid electrode.

In May, Prof. M. Seo and Mr. K. Fushimi attended the 8 th International Symposium on Passivity of Metals and Semiconductors held in Jasper, Alberta, Canada to present three papers entitled " Nanoindentation of Titanium Surface Covered with Anodic Oxide Film", " Localized Investigation and Modification of Passive Materials with the Scanning Droplet Cell", and " Heterogeneous Growth of Passive Film on a Polycrystalline Titanium Electrode Evaluated by a Scanning Electrochemical Microscope".

In June, Dr. A. W. Hassel (JSPS Foreign Researcher) attended the Gerischer Symposium on Semiconductor Electrochemistry held in Berlin, Germany to present the papar entitled "On the Cathodic Behaviour of InP in HCl" and also attended the Seminar at the Institute of Condensed Matter Physics held in Dueseldorf, Germany to present the papar entitled "Surface Energy and Stress Measurement in Thin Metal Film Electrodes using a Laser Beam Deflection and a Piezoelectric Response Method".

From August 30 to September 4, Prof. M. Seo and Assoc. Prof. K. Azumi visited Prof. Su-Il Pyun, Department of Materials Science and Engineering, Korea Advanced institute of Science and Technology (KAIST), Taejon, Korea to conduct the joint research of the stresses generated on transition metal electrodes during anodic oxidation and hydrogen absorption which was financially supported by JSPS and KOSEF, and Prof. M. Seo presented the KAIST seminar entitled " Stress Measurement of Iron and Titanium Electrodes during Anodic Oxidation".

In October, Prof. M. Seo, Assoc. Prof. K. Azumi , Mr. K. Fushimi , Dr. A. W. Hassel, and Mr. K. Ueno (Ph.D. Student) attended the Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan held in Hawaii, USA to present six papers entitled " Stability of the Anodic Oxide Film on

Titanium in Deaerated Neutral Solutions", "An EQCM Analysis of Passivation Process of Copper Thin Film", " Localized Photoelectrochemical Measurement with the Scanning Droplet Cell", " Local Analysis of Anodic Oxide Films on Titanium by Scanning Droplet Cell and Scanning Electrochemical Microscope", "Study on a Local Breakdown Process of Passive Film on Iron by a Liquid Phase-Ion Gun" and " Stress Measurement of the Iron Electrode Passivated in pH 8.4 Borate Solution". The International Symposium in Honor of Professor Norio Sato : Passivity and Localized Corrosion was held during the this Joint Meeting. On October 26, Dr. A. W. Hassel returned back to Germany to work with Prof. M. Stratmann at the Max Planck Institute für Eisenforschung GmbH after he accomplished his excellent postdoctoral research in this laboratory for two years.

The following foreign scientists visited this laboratory : Ms. Cuirong Bian, Shandong Medical University, China, Mr. Osama Ahmad Fouad, Central Metallurgical Research & Development Institute, Egypt, Ms. Anita Horvath, Institute of Isotope & Surface Chemistry, Hungarian Academy of Sciences, Hungary, Mr. Artur Malinowski, Institute of Physical Chemistry, Polish Academy of Sciences, Poland and Ms. Izabela Rzeznicka, Institute of General & Ecological Chemistry, Technical University of Lodz, Poland on July 2, Dr. Alexander Mozalev, Belarusian State University of Infomatics & Radioelectronics, Minsk, Belarus on July 8, Dr. Ma Li, Department of Science and Technology, Linkopings University, Sweden on September 30, Dr. Christina Bock, Insitute for Chemical Process and Environmental Technology, National Research Council Canada on December 7- 9.

Presentations

Evaluation of the Heterogeneity of Passive Films on Iron and Titanium by a Scanning Electrochemical Microscope; M. Seo and K. Fushimi: The 122 th Symposium on Corrosion Protection, Tokyo, Jan., 1999.

Electrochemical and Fundamental Study of the Light Emission Phenomenon from Electrode during Electrolysis ; M. Kawaguchi, K. Azumi, M. Seo and T. Mizuno : The 1999 Joint Meeting of Hokkaido Sec. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Corros. Eng., Sapporo, Jan., 1999.

Semiconductor Electrode Characteristics of InP in HCl and H3PO4 ; M. Aihara, A. W. Hassel and M. Seo: ibid.

Study on Anodic Oxidation and Electroluminescence Characteristics of Porous Silicon; M. Saito, A. W. Hassel and M. Seo: ibid.

Evaluation of Hydrogen AbsorptionIinto Ti Using Resistmetry ; Y. Asada, K. Azumi, M. Seo, T. Mizuno: ibid.

Effects of Additives on Zn Deposition in Zincate Pretreatment ; Y. Shindo, K. Azumi, M. Seo: ibid.

Comparison between Anodic Oxide Films Formed on Titanium in Neutral and Various Electrolyte Solutions;N. Yasui, K. Azumi and M. Seo:ibid.

Heterogeneous Growth of Anodic Oxide Films on Polycrystalline Titanium Electrode; T. Okawa, K. Fushimi, K. Azumi and M. Seo: ibid.

Hardness Measurement of Micro-area of Titanium Surface Anodically Oxidized; F. Nukaya, K. Azumi and M. Seo: ibid.

Mechanical Properties of Micro-area of Iron (100) Surface Electrochemically Controlled; M. Chiba and M. Seo, ibid.

An EQCM Analysis of Passivation Processes of Electroplated Iron and Copper Thin Films; H. Tsuda and M. Seo: ibid.

The Influence of Specific Adsorption of Iodide Ions on Piezoelectric Singals of Gold Electrode in Soultion Containing $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$; Y. Serizawa, K. Ueno and M. Seo: ibid.

Measurement of Membrane Potentials of Manganese Oxide and Nickel Hyroxide

Electrochemically Synthesized; M. Ushito and M. Seo: The 1999 Winter Meeting of the Hokkaido Sec. of Jpn. Soc. Anal. Chem. and Chem. Soc. Jpn., Sapporo, Feb., 1999.

Measurement of Changes in Surface Stress of Electroplated Iron Electrode Surface by a Laser-Beam Deflection Method; K. Ueno and M. Seo: ibid.

Application of Scanning Electrochemical Microscope (SECM) to Passive Metal Surfaces ; M. Seo and K. Fushimi: Hungarian Electrochemical Society Meeting, Budapest, Hungary, April, 1999.

Measurement of Changes in Surface Stress of Iron Electrode during Passivation; K. Ueno and M. Seo: The 66th Annual Meeting of Electrochem. Soc. Jpn., Yokohama, April, 1999.

Light Emission Spectra from Metals during High Voltage Cathodic Electrolysis ; K. Azumi, M. Seo, T. Mizuno: ibid.

Local Breakdown of Passive Film Formed on Iron by an Ion Gun in Liquid Phase ; K. Fushimi, K. Azumi, M. Seo : ibid.

Application of QCM to Corrosion Study; M. Seo: The 1999 Annual Meeting of Jpn. Soc. Corros. Eng., Chiba, May, 1999.

The Mechanism of Cathodic Corrosion of InP in Acidic Solutions ; A. W. Hassel, M. Aihara and M. Seo: ibid.

An EQCM Analysis of Passivation Process of Electroplated Copper Thin Film; Y. Tsuda and M. Seo: ibid.

Nano-Indentation of Titanium Surface Covered with Anodic Oxide Film; F. Nukaya, K. Azumi and M. Seo: ibid.

Heterogeneous Growth of Passive Films on Polycrystalline Titanium; T. Okawa, K. Fushimi, K. Azumi and M. Seo: ibid.

Light Emission Spectra from Metals and Alloys during High Voltage Cathodic Electrolysis ; K. Azumi, M. Kawaguchi, M. Seo, T. Mizuno : ibid.

Development of Liquid-Phase Ion Gun and Its Application to Local Breakdown of Passive Films on Iron; K. Fushimi, K. Azumi and M. Seo: ibid.

Nanoindentation of Titanium Surface Covered with Anodic Oxide Film; M. Seo, F.

Nukaya and K. Azumi : The 8 th Intern. Symp. Passivity of Metals and Semiconductors, Jasper, Canada, May, 1999.

Localized Investigation and Modification of Passive Materials with the Scanning Droplet Cell; A. W. Hassel and M. Seo: ibid.

Heterogeneous Growth of Passive Film on a Polycrystalline Titanium Electrode Evaluated by a Scanning Electrochemical Microscope; K. Fushimi, T. Okawa, K. Azumi and M. Seo: ibid.

On the Cathodic Behaviour of InP in HCl ; A. W. Hassel, M. Aihara, M. Seo: Gerischer Symposium on Semiconductor Electrochemistry, Berlin, Germany, Jun., 1999.

Surface Energy and Stress Measurement in Thin Metal Film Electrodes Using a Laser Beam Deflection and a Piezoelectric Response Method ; A. W. Hassel, K. Ueno, M. Seo: Seminar at the Institute of Condensed Matter Physics, Dueseldorf, Germany, Jun., 1999.

Mechano-Electrochemistry of Passivated Metal Electrode; M. Seo and K. Ueno: Symposium on Electrochemistry of Ordered Interfaces, Grant-in-Aid for Scientific Research on Priority Area from The Ministry of Education, Science, Sports and Culture , Kumamoto, Sept.,1999.

Stress Measurement of Iron and Titanium Electrodes during Anodic Oxidation; M. Seo and K. Ueno: KAIST Seminar, Taejon, Korea , Sept., 1999.

Stress Measurement of Titanium Anodic Oxide Films; M. Seo, K. Ueno, K. Fushimi and H. Habazaki: The 46 th Discussion Meeting of Materials and Environments, Fukuoka, Sept.,1999.

Local Generation of Chloride Ions by a Liquid-Phase Ion Gun and Local Breakdown of Iron Passive Film; K. Fushimi and M. Seo: ibid.

Piezoelectric Detection of Changes in Surface Energy of Platinum Electrode due to Specific Adsorption of Iodide Ions; Y. Serizawa, K. Ueno and M. Seo, The 77 th Fall Meeting of Japan Chemical Society, Sapporo, Sept.,1999.

An EQCM Analysis of Passivation Process of Electroplated Copper Thin Films in Borate Solutions of Different pHs; H. Tsuda and M. Seo: ibid.

Semiconductor Electrode Characteristics and Cathodic Decomposition Reaction of InP in HCl; M. Aihara, A. W. Hassel and M. Seo: ibid.

Stability of the Anodic Oxide Film on Titanium in Deaerated Neutral Solutions; K. Azumi, N. Yasui and M. Seo :,The 1999 Joint International Meeting of The Electrochemical Society and the Electrochemical Society of Japan, Hawaii, USA, Oct., 1999.

An EQCM Analysis of Passivation Process of Copper Thin Film; M. Seo and H. Tsuda : ibid.

Localized Photoelectrochemical Measurement with the Scanning Droplet Cell; A. W. Hassel and M. Seo: ibid.

Local Analysis of Anodic Oxide Films on Titanium by Scanning Droplet Cell and Scanning Electrochemical Microscope; A. W. Hassel, K. Fushimi, T. Okawa and M. Seo: ibid.

Study on a Local Breakdown Process of Passive Film on Iron by a Liquid Phase-Ion Gun; K. Fushimi and M. Seo: ibid.

Stress Measurement of the Iron Electrode Passivated in pH 8.4 Borate Solution; K. Ueno and M. Seo: ibid.

Cathodic Decomposition Reaction of InP in HCl; M. Seo, M. Aihara and A. W. Hassel: Research Meeting on Environment and Materials for the 21 Century, Institute for Materials Research, Tohoku University, Sendai, Nov., 1999.

DISSIMILAR MATERIALS INTERFACE ENGINEERING LABORATORY

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In September, Assoc. Prof. Lu Yuxian returned to College of Materials Science and Engineering, Shandong University of Technology, China. Mr. Luo Feng and

Mr. Son Gun Su entered the graduate school of Engineering, Hokkaido University. Mr Hayashi quitted the graduate school and became an Research Associate of the laboratory.

The research activities of the laboratory are directed to an understanding of the mechanism of the high temperature corrosion in super alloys, inter-metallic compounds and iron-based alloys, and to the development of the corrosion resistant alloys and corrosion protection of steels with a hot dipping method in sea-water front environment. 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 oxidation resistance of Ti-Al alloys with pre-sulfidation treatment

High temperature oxidation behavior of Ti-Al intermetallic compound with pre-sulfidation treatment, which forms an Al rich layer at the surface of the alloy, was investigated. Effect of the third element addition to the alloy on the oxidation behavior was extensively investigated.

(3) Effect of water vapor on high temperature oxidation of ferrous alloys

Oxidation behavior in Fe-Al and Fe-Si alloys under the atmosphere containing water vapor was studied. Acceleration of the oxidation was observed and its mechanism was investigated.

(4) Effect of Re coating on high temperature oxidation of super alloy

Re was coated on the surface of a super alloy, and the oxidation behavior of the alloy was examined. A new method for coating Re on the surface of alloys based on an electric plating was also investigated.

(5) Refinement of scrap aluminum alloys by filtration method

Scrap aluminum alloys in solid-liquid existing state were filtered by pressuring to flow through an alumina plate filter having holes with various diameters, and contained Fe was reduced due to the separation of a Fe base intermetallic compound.

(6) 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.

(7) 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.

(8) Galvanizing process of steels by two step hot dipping

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

(9) Pb-free solder

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

Presentations

A Novel Process to Improve High Temperature Oxidation Properties of TiAl Alloys using Sulfidation Processing; T. Narita : The Joint Seminar between Japan and Australia, Sydney, Australia, Jan., 1999.

High Temperature Corrosion of Fe-10mass%Cr Alloy in Oxygen Atmosphere Containing N_2 and H_2O; S. Hayashi and T. Narita : The 1999 Joint Meeting of Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Corros. Eng., Sapporo, Jan, 1999.

Study on Refinement of Aluminum Scrap - Making of Ceramic Filter -; T. Suzuki, T. Mitsueda, K. Honma, J. Tanaka and T. Narita : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,1999.

Formation of Rhenium Film on Super Alloy and its Oxidation Resistance; M. Shoji, H. Yoshioka, K. Ohsasa and T. Narita : ibid.

Effect of Temperature on High Temperature oxidation of Fe-Si Alloy; M. Fukumoto, S. Hayashi, S. Maeda and T. Narita : ibid.

Effect of Ni on Initial Stage of High Temperature Oxidation of Low Alloy Steel; K. Son, S. Maeda, S. Hayashi and T. Narita : ibid.

In-Situ Observation of Pb Free Solder Joint by Laser Microscope - Thermal Cycle Behavior of Metal-Solder Joint - ; H. Okada and T. Narita : ibid.

Analysis of Isothermal Solidification Process in Transient Liquid Phase Bonding of Ni; K. Ohsasa, T. Shinmura and T. Narita: Annual Meeting of Jpn. Soc. Promotion of Science, Sendai, Jan.,1999.

Effect of Cr Addition on Oxidation Resistance of TiAl Alloy with Sulfidation Treatment; T. Narita, M. yatagai, T. Izumi and T. Yoshioka : Annual Meeting of 123 Committee of Jpn. Soc. Promotion of Science, Mar.,1999.

Non-Destructive Evaluation by using Ultrasonic Micro-Spectroscopy; T. Narita :

Annual Meeting of The Dept. of Non-Destructive Test, Soc. of Machinery Industry, Mar., 1999.

Improvement of Oxidation Resistance of TiAl Alloy by Sulfidation Treatment; T. Narita, M. Yatagai and T. Izumu : Symposium on Advanced Research of Energy Technology 1999, Sapporo, Mar., 1999.

Effect of Addition of Minute Amounts of Elements on Corrosion Resistance of Hot Dipped Coating; J. Tanaka, T. Tamura and T. Narita : Annual Meeting of Jpn. Inst. Metals; Tokyo, Mar., 1999.

Effect of Water Vapor on High Temperature Oxidation of Fe-5mass%Al Alloy in Nitrogen-Oxygen Mixed Gas; S. Hayashi and T. Narita : ibid.

High Temperature Sulfidation Characteristics of Ni-13.5Co-20Cr-xMo(x=2, 4, 6, 8mass%) Alloy under Low Sulfur Pressure.; C. Fang, T. Narita, H. Yakuwa and M. Miyasaka : ibid.

Effects of Temperature and Si Concentration on Initial High Temperature Oxidation of Fe-low Si Alloy; M. Fukumoto, S. Hayashi, S. Maeda and T. Narita : ibid.

Sulfidation of TiAl-2X(x= V, Fe, Co, Cu, Nb, Mo, Ag, W) Alloy at 1173K ; T. Izumi, M. Yatagai, Y. Matsunaga, K. Nakagawa and T. Narita : ibid.

Oxidation of TiAl-2X(x= V, Fe, Co, Cu, Nb, Mo, Ag, W) Alloy with Sulfidation Treatment at 1173K ; T. Izumi, M. Yatagai, Y. Matsunaga, K. Nakagawa and T. Narita : ibid.

Initial High Temperature Oxidation of Low Alloy Steel Containing Minute Amount of Ni ; K. Son, S. Maeda, S. Hayashi and T. Narita : Annual Meeting of Iron and Steel Inst. Jpn., Tokyo, Mar.,1999.

Sulfidation Properties of TiAl Alloys at High Temperatures; T. Narita and T. Yoshioka : Korean Spring Meeting of CSE, Korea, May, 1999.

Oxidation Behavior of Fe-Al Alloys in Air Containing Water Vapor; T. Narita and S. Hayashi : Special Seminar in Pohang University, Korea, May, (1999).

Sulfidation Processing to Improve High Temperature Oxidation Properties of TiAl

Alloys; T. Narita, M. Yatagai and T. Izumi : Special Seminar in Chugnam University, Korea, May, 1999.

Analysis of Solidification Behavior of Al base Multi-Component Alloy; K. Ohsasa, M. Shoji and T. Narita : Annual Meeting of Jpn. Foundry Engineering Soc., Tokyo, May, 1999.

Solidification Analysis of Al-Si Alloy using Thermo-Calc; Y. Hisamatsu, K. Ohsasa and T. Narita : Annual Meeting of Hokkaido Sec. of Jpn. Foundry Engineering Soc., Hakodate, Jun, 1999.

Scale Structure Formed at Initial Stage of High Temperature Oxidation of Fe-low Si Alloy; The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, July, 1999.

Oxidation Resistance of Ni base Super Alloy with PVD Coating of Re; M. Shoji, H. Yoshioka, K. Ohsasa and T. Narita : ibid.

Effect of Third Element on Oxidation of TiAl-2X Alloy with Sulfidation Treatment; T. Izumi, J. Tanaka and T. Narita : ibid.

Reaction between Thermoelectric Device and Sn-Bi Eutectic Solder; A. Toriyama, H. Tanaka, B. Kitani and T. Narita : ibid.

Molecular Dynamics Simulation of Nucleation Process at the Solid/Liquid Interface ; H. Yasumoto, K. Ohsasa and T. Narita : ibid.

Sulfidation Properties of Ni-13.5Co-20Cr-(0~8mass%)Mo Alloys at 873K under Low Sulfur Pressures; C. Fang, T. Narita, H.. Yakuwa and M. Miyasaka : The 1999 Joint Internationl Meeting of Electrochemical Society , Oct., Honolulu Hawaii, 1999.

Sulfidation Processing to Improve High Temperature Oxidation Properties of TiAl Alloys; T. Narita, M. Yatagai and T. Izumi : ibid.

Evaluation for Sensitizing Degree of Stainless Steel based on Characteristics of Sound-Elasticity; T. Narita, K. Yasuda, K. Yoneyama, H. Sohma and H. Tanaka : Annual Meeting of Jpn. Soc. Non-Destructive Test, 1999.

In-Situ Observation of Pb Free Solder Joint by Laser Microscope ; H. Okada and T. Narita : Annual Meeting of Jpn. Weld Soc., Nov., 1999.

Evaluation of Elasticity and Poisson's Ratio of Sn-X (X = Pb, Bi, Ag, Zn) Eutectic Solder by using Ultrasonic Method; T. Narita, H. Tanaka, O. Munakata, M. taguchi and F. Luo : ibid.

Improvement of High Temperature Oxidation Properties of TiAl Alloys; T. Narita : Special Seminar in Inst. Mater. Res. Tohoku University, Sendai, Nov. , 1999.

Formation of Alloy Layer and its Corrosion Behavior of Coating by using Zn-Al-Mg-Si Alloy Bath; J. Tanaka and T. Narita : Annual Meeting of Jpn. Inst. Metals; Kanazawa, Nov., 1999.

Effect of N_2 and O_2 on High Temperature Oxidation of Fe-5mass%Al Alloy in the Atmosphere Containing Water Vapor; S. Hayashi and T. Narita : ibid.

Ni-Cr-S Phase Diagram and Sulfidation Mechanism of Ni-20mass%Cr Alloy at 873K under Low Sulfur Pressures; C. Fang, T. Narita, H.. Yakuwa and M. Miyasaka : ibid.

Effect of Water Vapor on Initial High Temperature Oxidation of Fe-low Si Alloy; M. Fukumoto, S. Hayashi, S. Maeda and T. Narita : ibid.

In-Situ Observation of Thermal Cycle Behavior in Sn base Alloy/Metal Joint; H. Okada and T. Narita : ibid.

Effect of Added Elements on Oxidation of TiAl with Sulfidation Treatment; T. Izumi and T. Narita : ibid.

Reaction Diffusion of Thermoelectric Device and Pb Free Solder (1); A. Toriyama, H. Tanaka, B. Kitani, K. Ohsasa and T. Narta : ibid.

Pre-sulfidation and Cr-addition to Improve Oxidation Resistance of Ti-Al Intermetallic Compounds at Elevated Temperatures; T. Narita, T. Izumi, M. Yatagai, T. Yoshioka, Y. Matsunaga, and K. Nakagawa : 14th ICC, South Africa, Nov., 1999.

Probabilistic Simulation of Grain Structure Formation of Casting; K. Ohsasa : International. Conference on Cutting Edge of Computer Simulation of Solidification and Casting, Osaka, Nov., 1999.

High temperature Corrosion and Corrosion Protection of Waste Incinerator; Annual Meeting of Jpn. Soc. Engineers, Dec., 1999.

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Foreign Researchers

Dr. S. Moon, Y. S. Lee and S. J. Choi

Current Activities

In March, Mr. Y. S. Lee and S. J. Choi left for Changwon University, Korea, after one-year stay as research associates. Dr. M. Sakairi came back from England at the end of July after one and half year sabbatical stay as a postdoctoral fellow at

UMIST. Mr. K. Mabuchi received a doctor degree by the thesis entitled " Corrosion and Protection of Steels for LiBr-Refrigerators" at the end of September. Mrs. Y. Arai joined as a DC course student in October. At the beginning of November, Dr. Sungmo Moon, who had been graduated from Prof. Su Il Pyun's laboratory in KAIST, Korea, joined as postdoctoral fellow supported by JSPS, and he will stay for two years working on the laser and AFM technology on aluminum. Mr. H. Watanabe also joined at the beginning of November as a researcher from Showa-Cabot Super Metal Co., and will stay for one year.

The research activity of the laboratory is still directed to a better understanding of structure and properties of anodic oxide films on aluminum and its alloys, and of the oxidation resistant materials at high temperatures. Surface processing of aluminum is also attempted by the deposition of metal and organic compound after laser irradiation and AFM processing.

Current topics on research are in the following:

(1) Local Ni-P electroless plating on aluminum alloys with a pulsed YAG laser

Aluminum-(Fe, Cu, Mg, Si, Mn) alloy specimens were anodized to obtain porous oxide films, and irradiated with a pulsed YAG laser in solutions containing Ni^{2+} / H_2PO^{2-} to remove the oxide film locally. The effect of alloying elements on the deposition of Ni-P during the subsequent electroless plating was examined. All the alloy specimens showed a Ni-P deposition only at laser-irradiated area, and a faster deposition of Ni-P than highly pure aluminum. Alloying elements exposed to the solution by laser irradiation may act as catalytic centers to enhance the Ni-P deposition.

(2) Surface processing of aluminum by laser irradiation

Aluminum specimens covered with barrier-type anodic oxide films were moved at a constant rate in solution to be irradiated locally with a pulsed YAG laser. After laser irradiation, the specimen was anodized again in a H_2SO_4 solution and then immersed in a chromic acid / phosphoric acid solution. Porous-type anodic oxide films grew radially only at the laser-irradiated area during anodizing, and the oxide film could be removed completely during immersion. The hemispherical trenches with several μm diameters were produced in the metal substrate. The formation of trenches and pores was also attempted by a combination of laser irradiation with electro-etching.

(3) Surface processing of aluminum with AFM probe abrasion

Aluminum specimen covered with a thin, barrier type oxide film was abraded with AFM probe in either air or solution to produce fine pattern on the surface. The trenches became deeper almost linearly with increasing the abrasion number. The rate of increase in the trench depth was much higher in Cu_2SO_4 solution than in air or distilled water.

(4) Hard anodizing and destruction of the anodic oxide film with laser irradiation

Aluminum specimens were anodized in H_2SO_4 solutions at 273-293 K to examine the hardness of anodic oxide films and to observe the film destruction by pulsed YAG-laser irradiation in solution. Anodizing in 30%-H_2SO_4 at 273 K gave a uniform growth of porous anodic oxide films with 600 micro-Vickers hardness. By monitoring the immersion potential, the time for the complete destruction of the oxide film could be determined accurately.

(5) Formation of Al / Nb-composite oxide films by MOCVD and anodizing

Aluminum specimen was initially covered with Nb_2O_5 film by a metal organic chemical vapor deposition (MOCVD) at different temperatures, and then anodized galvanostatically in a neutral borate solution. Anode potential rised linearly with time, and the rate of rising in potential for Nb_2O_5-coated specimens was much higher than that without coating. The electric capacitance of the anodic oxide films formed on specimens coated with Nb_2O_5 was twice as large as that on the specimen without coating.

(6) Formation of Al / Si-composite oxide films by sol-gel coating and anodizing

Aluminum specimen was initially coated with Si-oxide by sol-gel coating with a silicon alkoxide / ethanol mixture, and then anodized galvanostatically in a neutral borate solution. During anodizing of the Si-oxide coated specimen, two oxide layers grew at the interface between Si-oxide coating and the metal substrate: an inner Al_2O_3 layer and an outer Al-Si composite oxide layer. Silicon-bearing species was considered to transport inwards across the Al-Si composite oxide layer during anodizing. The electric capacitance of the anodic oxide films formed after SiO_2 was 20% larger than that without coating.

(7) Structural change of anodic oxide films on aluminum during potentiostatic anodizing

Aluminum specimens covered with a hydroxide film were initially anodized galvanostatically up to $E_a = 200, 300, 400$ V in a neutral borate solution at 40, 60, 80°C, and then the potential of specimens was kept at these values to examine the change in the structure of anodic oxide films during potentiostatic anodizing. All the anodic oxide films consisted of two layers: an outer crystalline Al_2O_3 layer and an inner amorphous Al_2O_3 layer. The thickness of the outer layer increased with time during potentiostatic anodizing, whereas the thickness of the inner layer remained constant. There were many voids in the outer layer, and the amount of voids was larger at lower temperatures and at higher potentials. The voids were repaired partially during potentiostatic anodizing.

(8) Local organic coating on aluminum with laser irradiation and electrophoresis

Aluminum specimens covered with porous anodic oxide films were irradiated with a pulsed YAG laser to remove the oxide film locally, and then poly-acrylate film was coated by electrophoretic deposition. The coating was obtained only at the laser-irradiated area, and the coating was thicker at higher anode potential.

(9) Interfacial reaction between Nb and $MoSi_2$

The interfacial reaction between Nb and $MoSi_2$ at high temperatures is being investigated. The aims are to clarify the mechanism of the interfacial reaction and to estimate the maximum application temperature of the composite. The reaction layer consisted of Mo_5Si_3 and Nb_5Si_3 layers, and the reaction path was clarified. Studies on the effects of inserting diffusion barriers such as W, Ti, SiC, and Al_2O_3 on the interfacial reaction are also in progress.

(10) Sintering and oxidation of metal disilicide by a spark plasma sintering method

A spark plasma sintering method is being applied for fabrication of fully dense metal disilicides ($CrSi_2$, $FeSi_2$, $CoSi_2$, VSi_2, TaSi, WSi_2, $NbSi_2$, $MoSi_2$). The aims are to clarify the mechanism of the spark plasma sintering and to fabricate disilicides having outstanding oxidation resistance. Sintering in all disilicides starts at almost identical temperature. This suggests that spark occurs between particles in the initial stage of sintering. Oxidation behavior of the disilicides is also being investigated.

(11) Accelerated oxidation of $MoSi_2$

In order to clarify the mechanism of accelerated oxidation and pesting in $MoSi_2$, low temperature oxidation behavior is being investigated. Simultaneous oxidation of Mo and Si, namely accelerated oxidation, and pesting are liable to occur in a temperature range from 673 to 1073 K and at defects such as pores and cracks. In addition, H_2O vapor in air accelerates the occurrence of pesting. As a result, using fully dense $MoSi_2$ hinders the accelerated oxidation and pesting. Recently, TEM observation of scales formed on $MoSi_2$ at low and high temperatures is being done. The microstructures of scales formed by simultaneous oxidation at low temperatures and the process in crystallization of SiO_2 scales at high temperatures are being investigated.

(12) High temperature oxidation of stainless steels in H_2O-containing atmospheres

In order to clarify the effects of H_2O vapor on the oxidation behavior of stainless steels in a hot rolling process, oxidation tests at 1473 K in $(N_2\text{-}3\%O_2)\text{-}H_2O$ atmospheres are being done. Kinetics for growth of external and inner scales and the effects of Cr and H_2O on oxidation behavior were clarified.

Other activities

Prof. H. Takahashi attended the 6th International Symposium on passivity of Metals and Semiconductors, held in Jasper, Canada in May, and presented a paper entitled " Fabrication of Fine Pattern Coil by Anodizing/Laser Irradiation /Metal Deposition." Prof. Takahashi was one of the organizers of " International Symposium in Honor of Prof. Norio Sato – Passivity and Localized Corrosion-" held at Honolulu, Hawaii in the 196th Meeting of Electrochem. Soc. in October, and presented a paper entitled " Reformation of Anodic Oxide Films on Aluminum after Destruction with Laser Irradiation in Solutions. - Effects of Anion and pH -". Dr. Sakairi also attended the Honolulu meeting and presented a paper entitled "Effect of Benzotriazole on Anodizing of 2024 Aluminum Alloy in Sulfuric Acid at Low Temperature".

In November, Prof. Takahashi and Dr. Sakairi visited three Universities in Europe, Free University, Brussels, Heinrich-Heine University, Juesseldorf, and

Palermo University, Palermo, and discussed with Profs. H. Terryn, J. Vereecken, J. W. Schultze, M.M. Lohrengel, H.H. Strehblow, F. Di Quarto.

Assoc. Prof. Kurokawa attended the 2nd International Symposium on Applied Plasma Science which was held at Osaka on 20-24 of Sep., and presented a paper entitled "Effects of Sputter-Deposited Materials (W, Ti and SiC) on Interfacial Reaction Between $MoSi_2$ and Nb". He also attended the 14th International Corrosion Congress, which was held at Cape Town, South Africa, on 27 of Sep.-1 of Oct., and presented a paper entitled "Oxidation Behavior of Fully Dense $MoSi_2$-SiC Composites Fabricated by In-Situ Synthesis". After the congress, he attended the 6th Japan-France Materials Science Seminar at Poitiers, France, on 4-6 of Oct. In the seminar, he presented a paper entitled "Synthesis and Oxidation Resistance of $MoSi_2$-SiC Composites".

Foreign researcher visited the IMSA- Laboratory is Dr. A. Mozalev, Belarusian State University of Informatics & Radioelectronics, Minsk, Belarus on 7 - 11 of July, and he gave a lecture entitled "Application of aluminum anodizing in electronics and microelectronics inducing Li Rechargeable Battery Component Fabrication".

Presentations

Effects of Anion and pH on Repairing of Anodic Oxide Films on Aluminum after Destruction with Laser Irradiation in Solutions. ; Y. Ohira, M. Sakairi, and T. Takahashi: The Joint Meeting of The Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn., and Jpn. Soc. Corros. Eng., Sapporo, Jan., 1999.

Formation of Al –Zr Composite Oxide Films by Sol - Gel Coating and Pore – filling Method; K. Watanabe, M. Sakairi, H. Takahashi, R. Hasegawa, S. Hirai, and S. Yamaguchi: ibid.

Study of Cu Electroless - prating Mechanism on Al at Laser Irradiated area: S. Chu, M. Sakairi, and H. Takahashi: ibid.

Morphology of Scale Formed on $MoSi_2$ at Low Temperatures; Lee Y. Seang, J. Kuchino, K. Kurokawa, and H. Takahashi: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan., 1999.

Effects of Pore, H_2O Vapor and Temperature on Accelerated Oxidation of $MoSi_2$; K. Kurokawa: Japan-Australia Joint Seminar on High Temperature Corrosion, Sydney, Australia, Jan., 1999.

Fabrication of $MoSi_2$-Based Materials by A Spark Plasma Sintering Method; K. Kurokawa: North Forum of The Hokkaido Sec. of Iron and Steel Inst. Jpn., Sapporo, Feb., 1999.

Local Surface Modification on Al by Laser Irradiation and Au Deposition; T. Kikuchi, M. Sakairi, H. Takahashi, Y. Abe, and N. Katayama: The Winter Joint Meeting of The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem., Sapporo. Feb., 1999.

Anodic Oxidation Behavior of Al in Diluted NaOH Solutions; T. Che, M. Sakairi, and H. Takahashi: ibid.

The Technology of Alumite is Still Modern Technology. ; H. Takahashi: The 1st

Surface Finishing and Corrosion Protection Seminar: Surf. Finish. Soc. Jpn., and Jpn. Soc. Corros. Eng., Sapporo, Mar., 1999.

Sintering Behavior of Metal Disilicides by A Spark Plasma Sintering Method; K. Kurokawa, N. Hata, and H. Takahashi: The 6th Meeting of Inst. of Applied Plasma Sci., Saga, Mar., 1999.

Factors Affecting Accelerated Oxidation of $MoSi_2$: K. Kurokawa, J. Kuchino, Lee Y. Seang, and H. Takahashi, Symposium on Advanced Research of Energy Tech., Sapporo, Mar., 1999.

High Temperature Oxidation of Silicides (Over View Presentation); K. Kurokawa: The 124th Annual Meeting of Jpn. Inst. Metals, Tokyo, Mar., 1999.

Structure of Scale Formed on $MoSi_2$ at Low Temperatures; Lee Y. Seang, J. Kuchino, K. Kurokawa, and H. Takahashi: ibid.

Structure of $BaTiO_3$ Film formed on Al by Sol-gel Coating; K. Watanabe, M. Sakairi, H. Takahashi, R. Hasegawa, and S. Hirai: ibid.

Fine Patterning on Al by Laser Irradiation and Au Electro Plating. ; T. Kikuchi, M. Sakairi, H. Takahashi, Y. Abe, and N. Katayama: The 98th Annual Meeting of Surf. Finish. Soc. Jpn., Tokyo, Mar, 1999.

Local Deposition of Ni-P on Al by Laser Irradiation and Electroless Deposition; S. Chu. M. Sakairi, H. Takahashi, K. Shimamura, and Y. Abe: The 66th Annual Meeting of Electrochem. Soc. Jpn., Yokohama, Apr., 1999.

Anodic Oxidation Behavior of MOCVD- TiO_2 Coated Al-Effect of Formation Rate of TiO_2 on Structure of Anodic Oxide Film and Its Dielectric Property: K. Miwa, M. Sakairi, and H. Takahashi, Zairyo-to-Knakyo '99. Chiba, May, 1999.

Fabrication of Fine Pattern Coil by Anodizing, Laser Irradiation, and Metal Deposition. : T. Kikuchi, M. Sakairi, and H. Takahashi, The 8th Intern. Symp. on the Passivity of Metals and Semiconductors, Jasper, Canada, May, 1999.

Sintering and Oxidation Behavior of Metal Disilicides; N. Hata, K. Kurokawa, and H. Takahashi: The Summer Joint Meeting of the Hokkaido Secs. of Jpn. Inst.

Metals and Iron and Steel Inst. Jpn., Muroran, July., 1999.

TEM Observation of Scale Formed on $MoSi_2$ at Low Temperatures; J. Kuchino, K. Kurokawa, H. Takahashi: ibid.

Formation of Ai- (Ti, Nb) Oxide Film by Sol-gel Coating and Anodizing.-To Develop Next Generation of Super Electric Capacitor -; H. Takahashi: Open Symposium of Electrochemistry of Ordered Interfaces, Kumamoto, July, 1999.

Pore – filling of Zr Sol – Gel Coated Porous Type Anodic Oxide Films on Al; K. Watanabe, M. Sakairi, H. Takahashi, K. Takahirio, S. Nagata, S. Hirai: The 46th Discussion Meeting of Jpn. Soc. Corros. Eng., Fukuoka, Sep. 1999.

Anodic Oxidation of Zr Sol – Gel Coated Al. – Effect of Heat Treatment on Growth of Anodic Oxide Film of Coated Material -; K. Watanabe, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, and S. Hirai: The 77th Autumn Meeting of Jpn. Chem. Nov., 1999.

Effects of Sputter-Deposited Materials (W, Ti and SiC) on Interfacial Reaction Between $MoSi_2$ and Nb; K. Kurokawa, G. Ochiai, Hi. Takahashi, S. Ohta, and He. Takahashi: The 2nd Int'l Sump. on Applied Plasma Sci., Osaka, Sep., 1999.

Oxidation Behavior of Fully Dense $MoSi_2$-SiC Composites Fabricated by In-Situ Synthesis: K. Kurokawa, K. Kurokawa, M. Ube, J. Kuchino, and H. Takahashi: The 14th Int'l Corros. Cong., Cape Town, Sep., 1999.

Laser Irradiation and Local Deposition on Anodic Oxide Films Formed on Al; H. Takahashi: The 56th Meeting of ARS, Tokyo, Sep., 1999.

Local Ni–P Deposition on Al Alloys by Anodizing, Laser Irradiation and Electroless Deposition.–Effect of Condition at Laser Irradiation -: S. Chu, M. Sakairi, H. Takahashi, K. Shimamura, and Y. Abe, The 100the Annual Meeting of Surf. Finish. Of Jpn., Nagoya, Oct., 1999.

Structural Change of Barrier Type Anodic Oxide Films on Al at Keeping Constant Potential; Y. Tamura, M. Sakairi, H. Takahashi, and H. Uchi: ibid.

Fine Pattering of Al Surface by Laser Irradiation and Electrochemistry: T. Kikuchi,

M. Sakairi, H. Takahashi, Y. Abe, and N. Katayama: ibid.

The Key Factor of Breakdown Voltage of Al Electrolytic Capacitor. - What is the Breakdown. ; H. Takahashi, M. Sakairi, and H. Shimada: The 16th ARS Biwa-ko conference, Nagahama, Nov., 1999.

Repairing of Anodic Oxide Films on Aluminum after Destruction with Laser Irradiation in Solutions. - Effects of Anion and pH -; H. Takahashi, M. Sakairi, and Y. Ohira: The 1999 Joint International Meeting, The Electrochem. Soc., and Electrochem Soc. of Jan., in Honor of Prof. Norio Sato: Passivity and Localized Corros., Honolulu, U. S. A., Oct. 1999.

Effect of Benzotriazole on Anodizing of 2024 Aluminum Alloy in Sulfuric Acid at Low Temperature; M. Sakairi, P. Skeldon, G. E. Thompson, G. C. Wood and K. Stevens: ibid.

Synthesis and Oxidation Resistance of $MoSi_2$-SiC Composites; K. Kurokawa, M. Ube, Hi. Takahashi, He. Takahashi: The 6th Japan-France Materials Science Seminar, Poitiers, France, Oct., 1999.

New Technology of aluminum by Anodizing, Laser Irradiation, and Electroless Plating; H. Takahashi: Belgium-Japan Joint Mini-Symp. on Aluminum Surface Science and Technology, Brussels, Belgium Nov., 1999.

Formation of Porous Type Anodic Oxide Film on 2024 Al-Cu Alloys; M. Sakairi, P. Skeldon, G. E. Thompson, G. C. Wood and K. Stevens: ibid.

Local Surface Modification of Aluminum with Laser Irradiation and Electrochemical Technique; H. Takahashi: Seminar at Heinrich-Heine-Universtat, Jusseldorf, Germany, Nov., 1999.

Destruction of Anodic Oxide Films on Aluminum by LASER Irradiation; M. Sakairi, Y. Ohira, Z. Kato and H. Takahashi, ibid.

Formation of Composite Oxide Films on Aluminum by Sol-Gel Coating and Anodizing: H. Takahashi, Seminar at Palermo University, Palermo, Italy, Nov., 1999.

High Temperature Oxidation Behavior of Metal Disilicides; N. Hata, K. Kurokawa, and H. Takahashi: The 125th Annual Meeting of Jpn. Inst. Metals, Kanazawa, Nov., 1999.

Observation of Scale Formed on $MoSi_2$ at Low Temperatures by TEM; J. Kuchino, K. Kurokawa, H. Takahashi: ibid.

Microstructure of Scale on $MoSi_2$ Formed at High Temperatures; S. Ohta, D. Gotoh, H. Takahashi, K. Kurokawa: ibid.

High Temperature Oxidation of Steels in H_2O–Containing Atmospheres; A. Yamauchi, K. Kurokawa, H. Takahashi, and K. Takada: ibid.

Sintering Behavior of Metal Disilicides by SPS; K. Kurokawa, N. Hata, and H. Takahashi: The 4th Meeting on Spark Plasma Sintering, Jyozankei, Nov., 1999.

Structure of Anodic Oxide Films Formed on 2024 Al –alloy; M. Sakairi: The lecture of Hokkaido Sec. of Surf. Finish. Soc. Jpn., Sapporo, Dec., 1999.

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The research activities cover (1)the development, evaluation and application of dental and biomaterials, (2)the development of methods and equipments for fabrication of materials and prostheses and (3)the measurement of properties. These are concerned with mechanical, thermal properties, corrosion, surface treatment, biocompatibility, bioreactivity, estheticity and various methods of imaging and microanalysis. Many researches are related to dental, biological and engineering fields and performed in collaboration with clinical departments including Removable Prosthetic Dentistry(Prof.Takao Kawasaki), Orthodontics(Ass.Prof.Tohru Imai), Operative Dentistry (Prof.Hidehiko Sano), Oral and Maxillofacial Surgery (Prof.Yasunori Totsuka), and Crown and Bridge Prosthodontics(Prof.Noboru Ohata).

Current topics on research are as follows;

(1) Development of functionally graded dental implant

The dental implant with the structure of functionally graded materials (FGM) has been fabricated to satisfy different properties. The typical example is such that the composition changes from the biocompatible metal, Ti, at one end, increasing the content of ceramics, hydroxyapatite (HAP), principal component of bone and teeth, toward 100% HAP at the other end. This can control the functions of mechanical properties and biocompatibility, optimize them, depending on the necessity of each part of implant, without the abrupt change by the formation of discrete boundary. The effect of FGM structure Ti/HAP, Ti/Co on tissue response is investigated by the animal implantation test into rats and rabbits. The tissue reaction and new bone formation around the implant to the gradient composition is evaluated by both the conventional method using an optical microscope with stained specimens and by elemental mapping and other imaging methods using electron microprobe analysis(EPMA) and X-ray scanning analytical microscope(XSAM) with unstained specimens.

(2) Development of FRP esthetic orthodontic wire

To realize the esthetic, transparent orthodontic wire the FRP wires of the diameter 0.5 mm with the multiple fiber structure has been fabricated by either drawing of fiber-polymer complex at 250°C or photopolymerization method. Biocompatible $CaO\text{-}P_2O_5\text{-}SiO_2\text{-}Al_2O_3$ (CPSA) glass fibers of 8-20 μm in diameter are oriented unidimensionally to the longitudinal direction in polymer matrix of PMMA, UDMA or bis-GMA. The improvement has been done to obtain the adequate flexural strength and higher torque. FRP wire shows the sufficient flexural strength and a very good elastic recovery. The dependence of Young's modulus and flexural stress on fiber fraction obeys very well the rule of mixture. This FRP wire can cover the range of the strength corresponding to the conventional metal orthodontic wires from Ni-Ti used in the initial stage of orthodontic treatments to Co-Cr used in the last stage by changing the volume ratio of glass fibers with the same external diameter. FRP wire can satisfy both mechanical properties and estheticity, which is not possible for the conventional metal wire.

(3) Evaluation of biocompatibility of refractory metals and their application

Refractory metals of IVA group(Ti, Zr, Hf), VA group(V, Nb, Ta) and VIIA group(Re) are investigated in their biocompatibility and other bioreactivities. Animal implantation tests show that the fraction of direct contact of newly formed bone to implant material without intervening of fibrous connective tissue at the interface and the amount of new bone vary depending on materials. The composites of these refractory metals are also made and the comparison and the composite effect is investigated.

(4) In situ observation of etching process of human teeth in acid agent by atomic force microscopy

Composite resin with fillers of ceramic powders in polymer matrix has estheticity similar to natural teeth color and is widely used for treatments of caries in incisal teeth. Physical-mechanical anchoring effect plays an important part in binding force between teeth and composite resin. The pretreatment to make etching of teeth is generally done using acid agents for enhancement of binding. SEM is usually used for the evaluation of etching effect. It can observe, however, only the result after a certain etching time. To observe the sequence of etching process it is necessary to prepare the series of specimens treated with different etching time. Atomic force microscope is applied for the in-situ observation of etching process of human enamel and dentin in acid agents. The chronological change of surface morphology can be successively observed and quantitative analysis is done for different etching conditions.

(5) Dental applications of acoustic emission technique

Fracture toughness of dental materials including more detailed discussions using an acoustic emission technique. Acoustic emission (AE) is employed to evaluate the microscopic and macroscopic aspects of mechanical behavior of metal-,ceramics- and polymers- based materials and their composite materials.

(6) Grafting of methyl methacrylate onto collagen using ferric chloride-N-phenylglycine

Graft polymerization of vinyl monomer onto human hard tissues has not been studied extensively, without tri-n-buthylborane initiated MMA-based materials.The purpose of this study was to grafting of MMA onto collagen using various ferric ions-N-phenylglycine as a redox initiator.

(7) Development of halide fluxes for titanium soldering

The reactivity of KHF_2-LiF-NaCl-KCl fluxes with titanium were examined. The reactivity of the fluxes were promoted in the order of (NaCl+KCl)<(56KHF_2-14LiF-30(NaCl+KCl))<(50KHF_2-50LiF)<(70KHF_2-30LiF)<(KHF_2)<LiF. The reactivity of the fluxes was not alway consistent with the increasing in the spreading areas of solder.

(8) Surface treatment of dental and biomedical materials with sol-gel method

Biocompatibility and adhesivity to tissue is important for dental materials.

Various dental metals were coated by amorphous silica gels with sol-gel method. In some cases, biocompatibility were improved.

(9) Tissues and dental materials observation by XSAM

The scanning X-ray analytical microscope (XSAM) was applied for the analysis of the soft tissue of rat in which various metals including Fe, Cu, SUS, V, Co, Ni were implanted. The dissolution of implanted metals and inflammation of tissues were observed by elemental mapping image obtained by XSAM.

Other activities:

The 34th General Meeting of the Japanese Society for Dental Materials and Devices(JSDMD) was held at University Conference Hall of Hokkaido University on October 8-10 under the Chairman of Prof.Watari. The largest numbers of presentations ever as JSDMD, 189 oral and poster presentations, were done from all over the fields of biomaterials, dental materials and devices. The special project: Joint Program between JSDMD and the Swedish Dental Society was organized under the subject of "Dental Materials and Devices in the Aged Society". As invited symposists from Umea University, Sweden, Prof.Bo Bergman made the presentation "System and experience in Sweden regarding home treatment, insurance and cooperation between hospital and dentists" in Night Session and Prof.Maud Bergman made the special lecture "Side effects of dental materials reported in Scandinavian countries". The contents of the latter are published as a review paper in Dental Materials Journal 19(1), 2000. Home Page for meeting informations (http://www.den.hokudai.ac.jp/rikou/jsdmd/index.html) was set up and the live relay of the night session, special lectures and symposium was broadcast by internet during the meeting.

The special programs were as follows:

*Night Session(Oct.8) "Dental clinics for the society of the elderly aged in the

21st century" including "Elderly aged society of the 21st century and quality of life" by Prof.Isamu Kaneko(Graduate School of Letters), "Cooperation among primary, secondary and third treatments" by Dr.Kazu Yamazaki(Hokkaido Dental Association), "Cooperation between university hospital and regional dentists" by Dr.Fumihiko Sato (Hokkaido Dental Association), "Ideal of home treatment and problems" by Miss Nanae Togashi(Hokkaido Society of Dental Hygienists, "Home treatment and dental technicians" by T.Takashi Osawa(Hokkaido Society of Dental Technicians), "System and experience in Sweden regarding home treatment, insurance and cooperation between hospital and dentists" by Professor Emeritus Bo Bergman (University of Umea,Sweden), "Development of devices for the aid of the elderly aged and the handicaped" by Dr.Shigeo Nishimura(Hokkaido Rehabilitation Counseling Center), "Society of the elderly aged and venture business" by Prof.Yasuyuki Hamada(Graduate School of Economics).

* Special lecture(Oct.9) "Man and soap bubbles-Observation of people in the paintings-" by Prof.Yoko Mori(Meiji University)

* Special lecture(Oct.9) "Side effects of dental materials reported in Scandinavian countries" by Professor Emerita Maud Bergman(University of Umea,Sweden)

*Symposium(Oct.10) "Dental Materials, Devices and Medical Science - Various Applications of Materials and Devices" including "Application of X-ray microanalyzer for medical science" by Associate Prof.Koichi Watanabe(Niigata University), "Application of laser lithography for maxillo-facial surgery" by Prof.Noboru Ohata(School of Dentistry), "Application of hydroxyapatite for adult disease" by Dr.Hideki Aoki(Institute of Bioceramics, Inc.) and "Development of the sensory aid systems for the disabled" by Prof.Tohru Ifukube(Research Institute for Electronic Science, Hokkaido University).

The international collaborations are continued with Institute of Dental Materials Science, Umea University, Sweden (Emerita Prof. Maud Bergman, Prof.Lars-Ake Linden) on application of Ti, ZrO_2 for dentistry, research on side effects and other subjects, and with Department of Dental Materials, Chonbuk National University, Korea (Prof.Tae-Sung Bae) on evaluation of mechanical properties of Ti, dental porcelain and other subjects.

Emeritus Prof.Bo Bergman of Department of Prosthetic Dentistry and Emerita Prof.Maud Bergman of Department of Dental Materials Science, Umea University, Sweden stayed on October 7-11 to participate as invited symposists in Joint Program between JSDMD and the Swedish Dental Society which was planned in the 34th General Meeting of JSDMD.

Prof.Tae-Sung Bae of Department of Dental Materials, Chonbuk National University (Korea), which is a sister school with Hokkaido University School of Dentistry, also attended the JSDMD meeting with his department members on Oct.8-11 and made plural presentations.

The collaboration with Division of High Temperature Materials Science of Institute for Materials Research, Tohoku University (Prof.Toshio Hirai, Dr.Mamoru Omori) is also undergoing on the fabrication of new biomaterials including composite materials and functionally graded materials by applying a spark plasma system(SPS) as a method to enhance sintering. The research on the surface treatment of Ti by sol-gel method and evaluation of cytotoxicity is developed in cooperation with Department of Materials Science and Engineering, Muroran Institute of Technology(Prof.Kazuyoshi Shimakage, Assoc.Prof.Shinji Hirai).

Presentations

Tissue response to laser-welded bi-implants composed of different refractory metals; H,Matsuno, A.Yokoyama, R.Miyao, F.Saso, T.Kawasaki, M.Uo, S.Ohkawa, T.Sugawara, S.Kondo, F.Watari: The 33th Jap.Dent.Mater.and Dev., Kawasaki, Apr., 1999.

Fabrication of rectangular esthetic orthodontic wires with torsional properties; H.Toyoizumi, S.Yamagata, K.Nagayama, M.Uga, T.Imai, S.Kondo, S.Ohkawa, M.Uo, T.Sugawara, F.Watari, M.Kobayashi: The 33th Jap.Dent.Mater.and Dev., Kawasaki, Apr., 1999.

The bracket form that reduces stress concentration of orthodontic wires; M.Uga, S.Yamagata, K.Nagayama, H.Toyoizumi, T.Imai, S.Kondo, S.Ohkawa, M.Uo, T.Sugawara, F.Watari, M.Kobayashi: The 33th Jap.Dent.Mater.and Dev., Kawasaki, Apr., 1999.

Effect of dimethylsiloxane segment-containning macromonomers on fracture toughness of heat cure type PMMA-based denture base resin; S.Kondo, S.Ohkawa, M.Uo, T.Sugawara, F.Watari: The 33th Jap.Dent.Mater.and Dev., Kawasaki, Apr., 1999.

Fabrication of dental prosthetic appliances with slip casting(Part 1); S.Ohkawa, K.Ishii, S.Kondo, M.Uo, T.Sugawara, F.Watari: The 33th Jap.Dent.Mater.and Dev., Kawasaki, Apr., 1999.

Observation of soft tissues implanted with metals by X-ray scanning analytical microscope and EPMA; F.Watari, H.Matsuno, A.Yokoyama, T.Kawasaki: The 55th Annual Meeting of the Japanese Society of Electron Microscopy, Nagoya, May, 1999.

Suppression of water absorption in esthetic FRP wire for orthodontics by coating; F.Watari, K.Nagayama, S.Yamagata, H.Toyoizumi, M.Uga, T.Imai, M.Uo, M.Kobayashi: The 1998 Annual Meeting of Jap.Soc.Corros.Eng., Chiba, May, 1999.

X-ray Diffraction Study of Carburization Transformation from Tantalum to Tantalum Carbide; F.Watari, M.Takahashi, K.Yada, Int.Conf.Solid-Solid Phase Transformations '99, Kyoto, May, 1999.

Fatigue test of an esthetic FRP orthodontic wire; M.Kobayashi, K.Yasuda, S.Ohkawa, F.Watari, T.Imai: The 34th Jap.Dent.Mater.and Dev.,Sapporo, Oct., 1999.

Solubility of the glass-fiber used for an esthetic FRP orthodontic wire; M.Kobayashi, M.Shibuya, M.Yamashita, Y.Toda, K.Hashimoto, F.Watari, T.Imai: The 34th Jap.Dent.Mater.and Dev.,Sapporo, Oct., 1999.

Deformational action of esthetic orthodontic wires in the bending test with an improved model bracket; M.Uga, S.Yamagata, K.Nagayama, H.Toyoizumi, T.Imai, S.Kondo, S.Ohkawa, M.Uo, T.Sugawara, F.Watari, M.Kobayashi: The 34th Jap.Dent.Mater.and Dev., Sapporo, Oct., 1999.

Properties of titanium-apatite composite fabricated by spark plasma sintering method; R.Miyao, A.Yokoyama, H,Matsuno, T.Kawasaki, M.Uo, S.Ohkawa, T.Sugawara, S.Kondo, F.Watari: The 34th Jap.Dent.Mater.and Dev., Sapporo, Oct., 1999.

Analysis of around soft tissue using titanium plate for bone fixation; R.Kumazawa, F.Watari, H,Matsuno, M.Uo, M.Oda, H.Yamaguchi, S.Nishikata, N.Inoue, Y.Totsuka: The 34th Jap.Dent.Mater.and Dev., Sapporo, Oct., 1999.

A basic study on manufacturing composite resin prostheses by laser lithography; S.Matsuo, N.Sato, Y.Ueda, N.Ohata, F.Watari: The 34th Jap.Dent.Mater.and Dev., Sapporo, Oct., 1999.

Cytotoxicity of titanium alloy coated with amorphous hydroxyapatote by sol-gel method; M.Uo, F.Watari, K.Nishinaka, S.Hirai: The 34th Jap.Dent.Mater.and Dev., Sapporo, Oct. 1999.

Polymerization of MMA monomer in the presence of human dentin disk using various ferric compounds-$NaHSO_3$ initiators; S.Kondo, S.Ohkawa, M.Uo, T.Sugawara, F.Watari: The 34th Jap.Dent.Mater.and Dev., Sapporo, Oct., 1999.

Gentle Dental Implants for Living Bodies; F.Watari: 14th Open Symposium on University and Science "New Materials in the 21st Century-Functionally Graded Materials Activating Industrial Worlds", Tokyo, Dec., 1999.

LABORATORY OF ADVANCED MATERIALS CHEMISTRY

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Most of our effort is devoted to the following topics on materials science and engineering.

(1) Formation and characterization of the composite materials of carbon, ceramics and metals

Various carbon composites were formed by carbonization of 1) polyimide films containing metal complexes, 2) powder mixtures of organic polymer and ceramics and 3) chelate resins complexed with metal ions. Basic researches on the structure, composition, electric and magnetic properties of composites are in progress by using XRD, TEM, SEM, Raman spectroscopy, SQUID, EIS, and others.

(2) Development of a new formation process of B/C and B/C/N composite materials

New precursors were found for production of title materials. They were prepared by chemical processes using the combinations of (a) sugars, polyhydric alcohols or the compounds containing *N*-glucamine functional groups and (b) boric acid or organoboranes. Carbonization of these precursors provided the B/C or B/C/N composites with high boron concentration. Preliminary characterization revealed that these composites show good oxidation resistance in a pure oxygen atmosphere.

(3) Synthesis and characterization of rare earth-chromium(V) compounds

Unusual chemical state compounds, $LaCrO_4$ and $Nd_{1-x}Ca_xCrO_4$ (x=0-0.2), were synthesized and their structures including atomic positions, composition, vibrational structures, electric properties, electron configurations were investigated in detail.

(4) Anodic oxidation of aluminum in metal-complexes solutions

Aluminum was anodized in the solutions containing complex anions of metals (Fe, Ti, etc.). Some of the solutions provided oxide films having interesting properties. Further investigation of these processes is in progress.

(5) Development of the surface finishing processes alternative to chromate treatment

New conversion coating solutions for metals were found using molybdate and metal salts. Coatings formed on steel were more protective to corrosion in an aerated salt solution than those formed by ordinary molybdate treatment. Further development of this process using different metal salts is in progress.

(6) Recovery of heavy oils by using carbon materials

Exfoliated graphite and carbonized fir fibers were found to have very high sorption capacity of oil and be excellent materials to recover heavy oils spilled in sea and natural water. With these materials, it is possible that sorbed oil can be recovered by filtration and the carbon materials can be used repeatedly after filtration.

(7) Application of bioremediation on the water quality control

Application of Mn-oxidizing bacteria to the removal of Mn ions from polluted water is in progress, paying attention to the effect of carbon fibers on the activation of bacteria.

Other activities:

This laboratory is funded until 2000 financial year by two large projects, "Creation of Functional Nano- and Micro-Spaces in Carbon Materials" by the Japan Society for the Promotion of Science (JSPS) and "Recovery of Heavy Oils by Using Carbon Materials" by the New Energy and Industrial Technology Development Organization (NEDO).

Prof. Attila Vértes, Eötvös Loránd University, Budapest, Hungary, visited this laboratory on 2-6 June. Joint projects with his laboratory on carbon materials and unnusual valence state compounds are continuing from 1998 financial year partly by the Grant-in Aid for Scientific Research (B) from the Ministry of Education, Science, Sports and Culture, Japan.

Dr. Frederique Goutfer-Wurmser finished her term as a JPSP Post-doctorate Research Fellow and returned to France in the end of August.

Prof. H. Konno attended the 50th ISE Meeting held in Pavia, Italy, on 5-10 September. He was nominated to a member of JSPS 117th Committee on the Carbon Materials in May.

Presentations

Bioremedeation of Manganese-rich Mine Water by Sediments Containing Manganese-oxidizing Bacteria; K. Sasaki, K. Kurosawa, and H. Konno:IBS '99, El Escorial, Spain, 1999.

Heavy Oil Sorption by Different Carbon Materials; M. Inagaki, H. Konno, N. Tazumi and M. Toyoda: 24th Biennial Conf. on Carbon, Charleston, USA, 1999.

S.T.M. Studies on Nanoscopic Defects Created by Slight Oxygen Plasma Treatment on Natural Graphite Surface; E. Bourelle, H. Konno and M. Inagaki: 24th Biennial Conf. on Carbon, Charleston, USA, 1999.

Sorption of Heavy Oil by Exfoliated Graphite; M. Toyoda, K. Moriya, J. Aizawa, H. Konno, and M. Inagaki: Environmental Technology for Oil Polution, Jurata, Poland, 1999.

Environmental Technology for Oil Polution; M. Inagaki, H. Konno, M. Toyoda, K. Moriya, and T. Kihara: Jurata, Poland, 1999.

Formation of Black Anodic Oxide Films on Al from Ti-complexes Solutions; H. Konno, and T. Takenaka: 50th Meeting of ISE, Pavia, Italy, 1999.

NS ELECTROCHEMICAL LABORATORY

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In 1995 Emeritus Professor Sato contributed as Chairman of the Organizing Committee toward "The International Symposium on Plant Aging and Life Prediction of Corrodible Structure" held on 14-19 May in Hokkaido University, Sapporo, Japan. In that year he was invited to present a plenary lecture entitled "The Stability of Localized Corrosion" at the 9th Asian-Pacific Corrosion Control Conference held on 5-10 November in Kaohsiung, Taiwan, R.O.C.

In 1996 Professor Sato participated in the 13th International Corrosion Congress held on 25-29 November in Melbourne to present a paper "Interfacial Ion-Selective Diffusion Layers and Passivation of Metals".

In 1997 Dr. Sato was invited to present a plenary lecture entitled "Potential-Dimension Diagram of Localized Corrosion" at the Symposium on Localized Corrosion and Environmental Cracking (SOLCEC) held on 22-24 January at the Indira Gandi Centre for Atomic Research in Kalpakkam, India. In that year he was also invited to contribute two key note lectures in electrochemistry and corrosion meetings in Europe; one was "Electrochemical Breakdown of Passive Films and Chloride-Pit Stability" presented at the Joint International Meeting on Electrochemistry held on 31 August-5 September in Paris, France, and the other was "Potential-Dimension Diagram of Localized Corrosion" read at the European Corrosion Congress (EUROCORR' 97) held on 22-25 September in Trondheim, Norway. In the same year he was further invited to present a key note lecture "Electrode Potential and Corrosion" at the 10th Asian Pacific Corrosion Control

Conference held on 27-31 October at Bali, Indonesia.

From 1997 to 1999 Dr. Sato served as one of the advisory members of the three year research project on "Electrochemistry of Ordered Interfaces" supported by Grant-in- Aid for Scientific Research on Priority Area from The ministry of Education, Science and Culture.

In 1998 Dr. Sato presented an invited lecture "The anodic Stability and Breakdown of Passive Films on Metals" at the 6th International Symposium on Advances in Electrochemical Science and Technology" held on 26-18 November in Chennai, India.

In 1999 Professor Sato participated in the 8th International Symposium on the Passivity of Metals and Semiconductors held on .10-14 May in Jasper, Canada, and read a paper "Ion-Selective Lust layers and Passivation of Metals". In the same year he attended the Joint International Meeting of the Electrochemical Society of U.S.A and the Electrochemical Society of Japan and joined in the International Symposium on Passivity and Localized Corrosion in Honor of Professor Norio Sato held on 19-21 October in Hawaii, U.S.A.

Furthermore, Dr. Sato contributed during these years a number of lectures to the domestic meetings on electrochemistry and corrosion science.

Effects of Rust Layers on the Corrosion of Metals

Norio Sato

Zairyou-to-Kankyo (Corrosion Engineering), **48**(4), 182-189 (1999)

Anodic metal dissolution produces hydrated metal salts concentrated at the anode interface and modifies the ion transport in the interfacial 67diffusion layer to be anion-selective or cation-selective. The anion-selective diffusion layer formed with monovalent chloride or hydroxide contributes to the formation of a chloride film and leads to either the chloride-film-induced passivation if the chloride is insoluble (e.g. Ag/AgCl) or the transition from the active state to the polishing state dissolution if the chloride is soluble (e.g. Fe/$FeCl_2$). The cation-selective diffusion layer formed with multivalent phosphate or sulfate ions leads to the formation of an oxide film, and thereby to the oxide-film-induced passivation of metal anode (e.g. Ni/NiO). Generally, rust layers are anion-selective in acidic solutions and cation-selective in basic solutions. Adsorption of multivalent oxoanions often changes the rust layer from an anion-selective to a cation-selective layer. The anion-selective rust layer accelerates the localized corrosion of metals; whereas, the cation-selective rust layer inhibits the localized corrosion. The bipolar rust ion-selective layer suppresses the anodic metal dissolution and leads to metal passivation. The cathodic oxygen reduction is allowed to proceed on p-type rust layers but is inhibited on n-type rust layers. (Japanese)

Inhibition of Copper Corrosion with Esters of 4- and 5-Carboxybenzotriazole

N.Huynh, S.E. Bottle, T. Notoya and D.P. Schweinsberg

Proc. 39th Annual Conference of Australasian Corrosion Association paper, 39-037, (1999)

A series of alkyl esters derived from a mixture of 4-and 5-carboxybenzotriazole have been studied as inhibitors for copper. At pH 0 the inhibition efficiency (IE) of the octyl ester mixture (4-CBTAH-OH and 5-CBTAH-OE) was approximately 98%(0.1 mM). This was considerably higher than that for benzotriazole (BTAH) (60%) under similar conditions. At pH 8 the IE was still sufficient (75% versus 90% for BTAH) to justify use of the octyl ester mixture. No ester hydrolysis was observed. Anti-tarnishing tests also showed that the octyl esters exhibited superior inhibition. Surface enhanced Raman scattering (SERS) indicated that the octyl esters, like BTAH, inhibited corrosion at low pH by chemisorption of the protonated species through an azole nitrogen. The increased IE at low pH is attributed to Van der Waals' forces of attraction adjacent octyl chains oriented away from the copper. SERS also suggests that at higher pH chemisorption is replaced by a sterically hindered polymeric complex less protective than chemisorbed $CBTAH_2^+$-OE. Polarisation curves also support change to a new protective mechanism. (English)

Inhivitive Effect of 4- and 5-Carboxybenzotriazole on Copper Corrosion in Acidic Sulphate and Hydrogen Sulphide Solutions

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

Corrosion Science, **41**, 685-697 (1999)

Commercial carboxybenzotriazole(CBT) usually consists of a mixture of the 4- and 5-substituted isomers and as such has been used to inhibit copper corrosion. Little work has been done on the inhibiting action of the individual compounds in different corrodents, and this paper describes their effect on the corrosion of copper in aerated acidic sulphate solution (pH=0 and 4), and in an aqueous sulphidising environment. Gravimetric and potentiodynamic polarisation methods were employed in the acid corrosion studies,whilst coulometry was used to analyse the surface products formed in the hydrogensulphide containing solutions. Finally, surface enhanced Raman scattering (SERS) spectroscopy was used to examine the initial interaction of the compounds with the copper surface in acidic solution. The coupon tests in aerated acidic sulphate showed that the inhibition efficiency of each isomer was pH, concentration, and time dependent. At lower pH the 5-isomer is by far the better inhibitor, and this behaviour continues at higher pH where 4-CBT promotes corrosion. The inhibition efficiency of the 5-isomer increased markedly with exposure time and this was attributed to the increase in thickness of the underlying oxide layer. SERS revealed the presence of a broad peak at approx. 250 cm^{-1} and this has been assigned to the Cu-N stretching mode, resulting from adsorption of CBT onto the copper surface, and subsequent coordination through a triazole nitrogen. The anti-tarnishing tests showed that whilst both isomers exhibited these properties, once again5-CBT was the superior inhibitor. (English)

In situ etching observation of human teeth in acid agent by atomic force microscopy

Fumio WATARI

J. Electron Microscopy, **48**(5), 537-544 (1999)

Atomic force microscope was applied to in-situ observation of etching process of human teeth by acid agents. The change of surface morphology was observed consecutively before and during etching for the same area in the same specimen. The course of the etching process in enamel from dissolution of smear layer just after injection of acid agent, appearance of enamel prizms and progress of demineralization were quantitatively analyzed for three fundamental acid agents of 2% phosphoric acid, 10% citric acid and 10% polyacrylic acid. Then the depth profile, etching amount, etching rate and thickness of smear layer were evaluated. Observation by scanning electron microscopy was also done and compared with the results by atomic force microscopy.

CRGHU

Localized "Ant's Nest" Corrosion in Copper Tubes by Aldehydes and Ketones

T. Notoya, K. Kawano and T. Ando

Journal of Copper and Brass Research Association, **39**, 30-37 (1999)

The localized ant's nest corrosion in copper tubes, which are widely used in refrigerating and air-conditioning units, has been detected during the early stage of service and in leakage tests conducted after manufacturing. The morphology of this corrosion is similar to ant's nest when viewed in cross section. The optical microscopic examination of cross sections show corroded parts with underlying labyrinth of interconnecting channels containing copper oxide in random micropath. This type of corrosion is caused by decomposition products from chlorinated organic solvents used to degrease the tubes and from some types of lubricant oil used during the copper tubing stamping process. More recently, volatile organic substances from vinegar-containing serasonings, adhesives from synthetic building materials, cosmetics and perfumes, woods, and insecticides are also suspected as corrosive agents. These decomposition products and volatile organic substances include carboxylic acids, aldehydes and alcohols. Localized corrosion was found in copper tubes in air-conditioning units that has been installed 2.5 years ago in the wooden-walled rooms. Gas chromatographic analysis of air contaminants in the rooms showed trace amounts of volatile organic substances such as formaldehyde, nonylaldehyde, methylbuthylketone, alpha-pinene, 3-carene, limonen, and C_{14}-C_{26} hydrocarbons. Among these substances, the aldehydes and the ketones were suspected to be the substance causing the copper corrosion. A simulation test was conducted in a humid atmosphere with 9 different types of aldehydes, 6 ketones, and alpha-pinen and also formic acid and methylformate for comparison. It was found that formic acid, methylformate, formaldehyde and propionaldehyde caused severe localized corrosion in copper tubes, whereas only fine and directional pits were formed in the presence of ketones and alpha-pinene. As for long chain alkylaldehydes, the penetration depth was very small compared with that of formic acid, and a thick copper-organic complex layer, metallic soap, formed on the copper tube surface. This layer may act as a corrosion barrier preventing further penetration. (Japanese)

Uptake of Copper Ions in Marine Algae

T. Notoya

"The Usage of Seaweeds for Environmental Protection" ed. by M. Notoya
Seibundo p. 93-100 (1999)

On one hand copper is an essential element for metabolic processes in marine algae,i.e.,in electron transport in photosynthesis and in various enzyme systems. On the other hand it is thought to be one of the most toxic elements to marine algae.This article addresses mechanisms of uptake of copper ions into an algae cell,a possible interaction at the interface of algae cell membrane / seawater and the release process of copper complex exduates. The effects of copper in seaweeds and toxicity of copper species to marine algae are also discussed. (Japanese)

Effect of Ultra-Violet Light Irradiation on Anodic Oxide Films on Titanium in Sulfuric Acid Solution

Toshiaki Ohtsuka and Tetsuo Otsuki

J. Electroanal. Chem., **473**, 272-278 (1999)

Photo-corrosion of a 9.2 nm thick oxide film of TiO_2 formed anodically on titanium was studied in 0.1 M sulfuric acid solution by in-situ ellipsometry during 325 nm ultra-violet (*uv*) light irradiation. The *uv* light irradiation induces a change of the oxide film which is observed by ellipsometry. From the change of the ellipsometric parameters, the thickness decrease of the oxide film is estimated. The results estimated indicate that 5% of photo-induced current is consumed for photo-corrosion of the oxide film. The photo-corrosion rate is proportional to the positive bias relative to the flat-band potential and to the *uv* light intensity. The mechanism of the photo-corrosion is discussed for the photo-effect of an n-type semiconductive oxide electrode: the photo-corrosion is induced by an accumulation of photo-excited holes at the oxide surface, probably because the accumulation may increase the interfacial potential difference at the oxidel solution interface and weaken the Ti-O bond of the oxide. (English)

Evaluation of Heterogeneity in Thickness of Passive Films on Pure Iron by Scanning Electrochemical Microscopy

K. Fushimi, K. Azumi and M. Seo
ISIJ International, **39**(4), 346-351(1999)

Scanning electrochemical microscopy (SECM) was applied to evaluate the heterogeneity of a passive film formed on a pure iron electrode in deaerated pH 8.4 borate solution. A probe current image of SECM was measured with a tip-generation / substrate-collection (TG/SC) mode in deaerated pH 8.4 borate solution containing 0.03 mol dm^{-3} $Fe(CN)_6^{4-}$ as a mediator. The difference in thickness of passive films formed on two iron plates at different potentials could be evaluated from the probe current image. The probe current image of the passivated iron surface with distinctive crystal grains was composed of the patch patterns, the shapes of which coincided completely with the shapes of the substrate crystal grains. The probe current flowed above the grain surface oriented to {100} plane was less than that above the grain surface oriented to {110} or {111} plane. The grain orientation dependence of probe current was ascribed to the difference in thickness of passive films formed on the crystal grains. (English)

Evaluation of Heterogeneity of Passive Films Formed on Iron and Titanium Surfaces by a Scanning Electrochemical Microscope

M. Seo and K. Fushimi

Proceedings of the 122 nd Symposium of Corrosion and Protection,
p. 59-66 (1999)

A scanning electrochemical microscope (SECM) is capable of evaluating the heterogeneity in a mezoscopic area of electrode surface. In this review article, the principle and measurement modes of SECM were described and the SECM results of passive films on iron and titanium surfaces were shown as typical examples. Both the probe current images of passive films on iron and titanium indicated clearly that the thickness or defective structures of passive films depended on the substrate grains. Moreover, the improvement of lateral resolution in SECM, the more accurate measurement of probe current, the suitable choice of redox couple as a mediater and so on were discussed for the more powerful and useful application of SECM to the corrosion field. (Japanese)

Use of Ion Gun in Liquid Phase for Local Breakdown of Passive Film on Iron

K. Fushimi, K. Azumi and M. Seo

Proceedings of Critical Factors in Localized Corrosion III,
ECS, PV 98-17, 626-634 (1999)

An ion gun in liquid phase for the investigation of precursor processes of pitting corrosion was realized by using a silver/silver chloride microelectrode. It was used to induce a local breakdown of the passive film on iron. This electrode was set as a probe electrode of a scanning electrochemical microscope (SECM). A small amount of chloride ions was generated by cathodic polarization of the silver/silver chloride microelectrode and induced the local breakdown of the passive film formed on iron in deaerated pH 6.5 borate buffer solution. Moreover, the microelectrode could detect ferric ions dissolved at the initial stage of film breakdown. (English)

Application of Quartz Crystal Microbalance to Corrosion Research

Masahiro Seo

Zairyo-to-Kankyo, **48**(10), 610-620 (1999)

A quartz crystal microbalance (QCM) is capable of detecting small mass changes in the order of nano-grams from the changes in resonant frequency of a quartz oscillator. This article dealt with the principle of QCM and its application to corrosion research such as atmospheric corrosion and aqueous corrosion of metal thin films.

The corrosion kinetics and mechanisms of copper and iron thin films were discussed on the basis of typical results obtained by QCM combined with Auger electron spectroscopy and / or electrochemical technique. It was stressed that the heterogeneous corrosion, the stress generated in the film and the changes in the interfacial properties (viscosity and density) have to be taken into consideration as the factors influencing the resonant frequency which would provide the apparent mass changes. Moreover, the attempt to evaluate the vibration states of the quartz oscillator from the analysis of electrical equivalent circuit was introduced with respect to the deliquescence phenomena of salts adhered to the surface. (Japanese)

Electrochromism of Anodic Oxide Film on TiN Coating in Aqueous and Non-aqueous Electrolytes

Kazuhisa Azumi, Yutaka Kageyama and Masahiro Seo and Yukio Inokuchi

Thin Solid Films, **348**(1-2), 134-140 (1999)

Electrochromism of an anodic oxide film formed on a TiN coating was investigated in both a neutral borate buffer aqueous solution and a propylene carbonate solution containing $LiClO_4$. The TiN coating was prepared on Pt or stainless steel substrates, and was oxidized by anodic polarization in aqueous solution. The color of the TiN surface changed from gold to black when H^+ or Li^+ was absorbed into the oxide layer during cathodic polarization, and it turned to gold when H^+ or Li^+ was released during anodic polarization. Spectroscopic reflectance measurements showed that light absorption occurs in the whole visible range during coloring. In the aqueous solution, the time responses of coloring and bleaching processes were shorter than 1 s in the case of a fresh oxide layer. When the coloring / bleaching cycle was repeated over a long period, the response was delayed due to oxide layer thickening. AFM observation showed that the coloring / bleaching cycling was accompanied by the surface roughening, which would decrease the lifetime of TiN as an electrochromic device in an aqueous solution. In the non-aqueous solution, the time response of coloring and bleaching was slow, suggesting that the accumulation of Li in the oxide layer degrades the electrochromic property considerably. (English)

Experimental Determination of N 1s/C 1s Relative Sensitivity Factor for XPS

H. Konno and M. Inagaki

Anal. Sci., **15**, 799-801 (1999)

The relative sensitivity factor of *s*[N 1s]/*s*[C 1s] for semi-quantitative analysis by X-ray photoelectron spectroscopy (XPS) was determined using carbonized polyimide films. Good linear relationship was observed between fifteen data of the integral peak intensity ratio of N 1s/C 1s and the N/C atomic ratio by elemental analysis, an interrelation coefficient was 0.976. From this, *s*[N 1s]/*s*[C 1s] was estimated to be 1.751±0.079 (99% confidence limits). (English)

Influence of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ Redox Reaction on the Changes in Surface Energy of a Gold Electrode in Perchlorate Solution with Iodide Ions

K. Ueno, Y. Serizawa and M. Seo

Electrochemistry, **67**(12), 1123-1125 (1999)

Two novel technique of piezoelectric detection and laser-beam deflection were employed to examine the influence of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox reaction on the changes in surface energy of a gold electrode in perchlorate solutions with and without iodide ions. In the absence of iodide ions, both piezoelectric signal curve and electrocapillary curve suggested the specific adsorption of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ or some intermediates on the gold electrode. On the other hand, in the presence of iodide ions, it was found that the strong specific adsorption of iodide ions on the gold electrode inhibits the adsorption of the redox couple or some intermediates. (English)

In-situ Nanoindentation of a Single Crystal Iron (100) Surface Passivated in pH 8.4 Boric-Borate Solution

M. Seo, M. Chiba and K. Suzuki

Proceedings of Critical Factors in Localized Corrosion III,
ECS, PV 98-17, 1-10 (1999)

In-situ nanoindentation tests by using a Berkovich pyramidal diamond indenter were performed to examine the mechanical properties of single crystal iron (100) surfaces either cathodically reduced or passivated at 0.0 V and 1.0 V (SHE) for 1 h in pH 8.4 borate solution. The load-depth curves measured at a maximum load, Wmax = 50 μN and a load speed of 50 μNs^{-1} showed an evidence of plasticity irrespective of the electrochemical conditions for surface control. The hardness of iron surface calculated from the unloading curves ranged from 24 GPa to 50 GPa in the order: passivation at 1.0 V > cathodic reduction > passivation at 0.0 V. The indent shape after the indentation at a maximum load, W_{max} = 200 μN and a load speed of 20 μNs^{-1} for the iron surface passivated at 1.0 V was spreaded and became obscure with time, which was ascribed to active dissolution of iron near and under the indenter, followed by repassivation. (English)

Light Emission from Pt during High Voltage Cathodic Polarization

K. Azumi, T. Mizuno, T. Akimoto, T. Ohmori

J. Electrochem. Soc., **146**(9), 3374-3377 (1999)

Light emission from cathodically polarized Pt electrodes was investigated at cell voltages up to 200 V in aqueous electrolyte solutions. The emission of light was observed when intense cathodic polarization caused the temperature of the Pt electrodes to exceed the boiling temperature of the electrolyte: a thin vapor layer was formed at the metal electrolyte interface in which a high electric field ionized vapor molecules to generate a plasma state. The emission of light was caused by the glow discharge at relatively low cell voltages and by the spark discharge at high cell voltages. The spectra of the emitted light were assigned to the constituents of the electrolyte solution, electrode material and gaseous hydrogen evolved at the electrode. (English)

Light Emission Spectroscopy from Metal Electrodes during Electrolysis

Kazuhisa AZUMI, Masahiro SEO and Tadahiko MIZUNO

Electrochemistry, **67**(4), 349-354 (1999)

Light emission from the metal electrodes cathodically polarized at cell voltages up to 250 V was investigated in various aqueous electrolyte solutions. The light emission was observed when the temperature of electrodes exceeded the boiling temperature of the electrolyte due to the intense cathodic polarization : a thin vapor layer was formed at the metal / electrolyte interface in which a high electric field ionized vapor molecules to generate the plasma state. The light emission was caused by a glow discharge at relatively low cell voltages and by a spark discharge at high cell voltages. The spectra of the emitted light were assigned to the constituents of the electrolyte solution, electrode material and gaseous hydrogen evolved at the electrode. (Japanese)

Localized investigation of coarse grain gold with the scanning droplet cell by the Laue method

Achim Walter Hassel and Masahiro Seo

Electrochimica Acta, **44**(21-22), 3769-3777 (1999)

A coarse grain gold specimen was investigated using the scanning droplet cell (SDC). Voltamograms on single grains were obtained and show the shape which is characterisitic for a (111) single crystal plane. The potential dependence of the capacity was recorded as well. The crystallographic orientation of each grain was determined by the Laue X-ray back scattering. All grains have a (111) orientation but different azimuth angles. this angle was determined quantitatively for different grains. SEM micrographs show that the bredth of the grain boundaries is some 12 µm. The terraces of the grain and the grain boundaries were investigated by scanning impedance measurements using the SDC. Three different droplet diameters (50, 100 and 250 µm) were used. The grain boundary could be detected with all cells. The local capacity within the grain boundary was determined from this experiment. It is found to be 60 % higher than of the grains themselves probably due to the enlarged area within the ditch. The structure of the specimen is discussed and a model describing the results is presented. (English)

A coarse grain gold specimen was investigated using the scanning droplet cell (SDC). Voltamograms on single grains were obtained and show the shape which is characterisitic for a (111) single crystal plane. The potential dependence of the capacity was recorded as well. The crystallographic orientation of each grain was determined by the Laue X-ray back scattering. All grains have a (111) orientation but different azimuth angles. this angle was determined quantitatively for different grains. SEM micrographs show that the bredth of the grain boundaries is some 12 µm. The terraces of the grain and the grain boundaries were investigated by scanning impedance measurements using the SDC. Three different droplet diameters (50, 100 and 250 µm) were used. The grain boundary could be detected with all cells. The local capacity within the grain boundary was determined from this experiment. It is found to be 60 % higher than of the grains themselves probably due to the enlarged area within the ditch. The structure of the specimen is discussed and a model describing the results is presented. (English)

Nano-mechano-electrochemistry of iron (100) surface in solution

Masahiro Seo, Makoto Chiba and Kakunari Suzuki

Journal of Electroanalytical Chemistry, **473**, 49-53 (1999)

In-situ nanoindentation test by using a Berkovich pyramidal diamond indenter was performed to examine the mechano-electrochemical properties of single crystal iron (100) surface passivated at a constant potential for 1 h in pH 8.4 borate solution. The load-depth curve measured at a maximum load, $W_{max} = 50$ μN and a load speed of 50 μN s^{-1} showed an evidence of plasticity irrespective of the potential at which the passive film was formed. The average hardness of iron surface obtained from the unloading curve ranged from 2.0 GPa to 2.5 GPa and it increased with increasing the potential in the passive region higher than 0.25 V (SHE), indicating that the passive film contributes to the increase in hardness of the iron surface.

Moreover, the indentation at a maximum load, $W_{max} = 200$ μN and a load speed of 20 μN s^{-1} was performed in order to observe the time variation of shape of indent with AFM after the indentation. The indent shape for the iron surface cathodically reduced did not change significantly with time after the indentation. In contrast, the indent shape for the iron surface passivated at 1.0 V was spreaded and became obscure with time, which was ascribed to the active dissolution of iron near and under the indenter, followed by the repassivation. (English)

Photoelectrochemical Response and Stability of Titanium-Zinc Mixed Oxide Films Formed by Thermal Oxidation

Isao Saeki, Jun Setaka, Ryusaburo Furuichi, and Hidetaka Konno

J. Electroanal. Chem., **464**, 238-244 (1999)

The photoelectrochemical properties of titanium-zinc mixed oxide films formed by thermal oxidation of a titanium sheet with a zinc deposited overlayer were studied in pH 8.4 borate buffer solution at 298 K. The oxides were composed of ZnO (wurtzite), TiO_2 (rutile), and $ZnTi_2O_4$ depending on the oxidation temperatures. Under xenon light illumination, photocurrents were observed for the oxides and these values were higher than that of thermally formed titanium oxides. The photocurrent action spectra showed that the apparent bandgap energies of the oxides were similar to that of ZnO suggesting most of the photo-response is due to this compound. It was found that only a small amount of zinc ions were dissolved after long term photoelectrolysis indicating that the oxides are resistant to photo-induced dissolution. This may be explained by the formation of a surface titanium oxide rich layer left by partial dissolution of zinc ions.

Potential Modulation Reflectance of Self-Assembled Naphthoquinone Monolayers on Gold Electrodes

Toshiaki Ohtsuka, Morio Nagata, Hirokiyo Komori, and M. Nango

Electrochemistry, **12** (7), 1184-1186 (1999)

Potential modulation reflectance (PMR) was measured as a function of potential and wavelength of light for self-assembled monolayers (SAMs) formed from dialkyl disulfide-linked naphthoquinones with different spacer alkyl chain on a gold electrode. On the cyclic voltammogram a redox reaction between naphthoquinone and anphtho-hydroquinone in the SAMs is clearly observed. The oxidation and reduction peak currents are strongly dependent on the spacer alkyl chain length. On the PMR spectra two peaks are observed: one at 470 nm wavelength originates from the redox change between the naphthoquinone and naphtho-hydroquinone and the other peak 530 nm wavelength may be due to formation of a charge transfer complex between naphthoquinone and naphtho-hydroquinone. From the phase retardation of PMR and differential capacitance, it is supposed that relatively slow process like a configuration change of the naphthoquinone derivative accompanied by proton transfer are included in the redox reaction. (English)

Preventing Photoelectrochemical Corrosion of ZnO by Ti Inclusion

Isao Saeki, Jun Setaka, Ryusaburo Furuichi

Electrochemistry, **67**, 760-764 (1999)

Zinc oxide films containing small amounts of Ti oxide were prepared by heat treatment of Ti sheets with a Zn plated overlayer. Long term photoelectrochemical corrosion tests of the film at a constant potential of 1 V vs. Ag|AgCl was carried out. It was found that Zn^{2+} ions initially dissolved into the electrolyte solution but that dissolution then stopped. This behavior can be explained by an increase in the surface concentration of Ti. After some dissolution of Zn, the increased Ti concentration enables the surface to withstand further photoelectrochemical corrosion. This Ti containing oxide film showed a much better photoresponse than that of Ti oxide alone in the long wavelength region and would be a good candidate for photo anodes in aqueous electrolytes. (Japanese)

Selective Ion Permeability of Manganese Oxides Prepared with an Electrosynthesis

Miki Ushito and Masahiro Seo

Electrochemistry, **64**(4), 377-380 (1999)

The membrane potentials of γ-MnO_2 and Mn_3O_4, which were electrochemically prepared on Pt mesh, were measured in neutral aqueous solutions of KCl, KNO_3, NaCl and Na_2SO_4 at 25°C to examine the transport numbers of the electrolyte ions in the Mn oxides. In these solutions, the cation transport numbers, t_+ , in γ-MnO_2 were 0.62~0.73, which were larger than those (0.38~0.51) in the bulk solutions. On the other hand, the anion transport numbers, t_- , in Mn_3O_4 were 0.62~0.79, which were larger than those (0.49~0.62) in the bulk solutions. The above results indicated that γ-MnO_2 was cation-selective, whereas Mn_3O_4 was anion-selective. The difference in selective ion permeability between γ-MnO_2 and Mn_3O_4 was explained in terms of the difference in sign of surface electric charge, depending on zero point of charge (zpc) of Mn oxides and pH of the used solutions. (Japanese)

Selective Ion Permeabilities of $Ni(OH)_2$ and NiOOH Prepared with an Electrosynthesis

Miki Ushito and Masahiro Seo

Journal of the Surface Finishing Society of Japan, **50**(11), 62-66 (1999)

Membrane potentials of α-$Ni(OH)_2$ and β-NiOOH electrochemically prepared on Pt mesh, were measured in neutral aqueous solutions of KCl, KNO_3, NaCl and Na_2SO_4 at 25°C to determine the transport number of electrolyte ions in nickel hydroxide and oxy-hydroxide. The anion transport number, (t_- = 0.99 - 0.93), in α-$Ni(OH)_2$ was larger than that (t_- = 0.62 - 0.49) in the bulk solutions, indicating that α-$Ni(OH)_2$ has high selective anion permeability. On the other hand, the anion transport number, (t_- = 0.64 - 0.51),in β-NiOOH was not significantly different from that in the bulk solutions, indicating that β-NiOOH has low selective anion permeability.This low selective anion permeability may be attributed to the low positive fixed charge density of β-NiOOH in the measured solutions. (Japanese)

Study of Adsorption of Iodide Ions on Gold Electrode by a Laser Beam Deflection Method Compared with a Piezoelectric Technique

Kaoru Ueno and Masahiro Seo

J. Electrochem. Soc., **146**(4), 1496-1499 (1999)

Absolute values of changes in surface energy of gold electrode in perchlorate solutions with and without iodide ions could be measured by a laser beam deflection method. The potential of electrocapillary maximum or potential of zero charge (pzc) obtained by the laser beam deflection method was in good agreement with that obtained previously by a piezoelectric technique. The derivative of surface energy with electrode potential, $-(\partial\gamma^{s}/\partial E)$, was quite different from the surface charge density, q_m, obtained with integration of current density in the cyclic voltammogram, indicating that the simple Lippmann equation, that is, $-(\partial\gamma^{s}/\partial E) = q_m$, did not hold. Particularly, $-(\partial\gamma^{s}/\partial E)$ took a maximum near the potential at which the charge transfer of adsorbed iodide ions occurred to form the iodine adlayer in spite of that qm increased monotonously with increasing the potential. The above results obtained by the laser beam deflection method were also consistent with those obtained previously by the piezoelectric technique. The rapid decrease in $-(\partial\gamma^{s}/\partial E)$ after the charge transfer of adsorbed iodide ions is directly associated with the formation of the iodine adlayer. The discrepancy between $-(\partial\gamma^{s}/\partial E)$ and qm was ascribed to the changes in surface elastic strain accompanied by the structural changes of the adlayer. (English)

Surface Hydroxyl Site Densities on Metal Oxides as a Measure for the Ion-Exchange Capacity

Hiroki Tamura, Akio Tanaka, Ken-ya Mita, and Ryusaburo Furuichi

J. Colloid Interface Sci., **209**, 225-231 (1999)

Hydroxyl groups on metal oxide in water are the sites for ion exchange, and the surface hydroxyl site density on oxides is a measure of the ion-exchange capacity. Here, the Grignard reagent method was applied to determine the surface hydroxyl site density of oxide samples. The results were similar to those reported for different oxides with other methods (dehydration by heating, tritium exchange, crystallographic calculations, etc.), and they are comparable with that calculated from the closest packing of hydroxide ions. A mechanism of hydroxylation is proposed: lattice oxide ions (extremely strong bases) are exposed to aqueous solutions and are neutralized by water to become hydroxide ions. Also, the saturated deprotonation method was applied to hematite, and it was found that all the acid hydroxyl groups on hematite were deprotonated in very high concentrations of alkali solutions (~ 5 mol dm^{-3} NaOH), and from the saturated amount of OH^- consumed by deprotonation, the same result as that by the Grignard method was obtained. It is shown that all hydroxyl groups take part in ion exchange and that the unusually small values reported elsewhere with the saturated(de)protonation method may contain errors. Hetero- or homogeneity of hydroxyl groups in contact with water as ion-exchange sites is also discussed. It is suggested that intensely hydrated layers at the oxide/water interface may result in homogeneous discrete sites. The development of microstructures in the oxides was suggested from the measured values of specific surface areas, and the effect of the microstructure environments on the reactivity of internal surface hydroxyl sites is discussed. (English)

Surface Hydroxyl Site Density on Spinel-type λ-MnO_2 as a Measure of Ion-Exchange Capacity

A. Tanaka, H. Tamura, and R. Furuichi

Electrochemisty, **67**(10), 974-978 (1999)

Lambda-manganese dioxide (λ-MnO_2), a spinel-type oxide, has lattice vacancies with a size equal to that of lithium ions, and incorporates lithium ions selectively from aqueous solutions. Oxide surfaces in water are hydroxylated by hydration, and the surface hydroxyl groups adsorb ions non-selectively by ion exchange, interfering with the selective incorporation of lithium ions. In this investigation, the surface hydroxyl groups on λ-MnO_2 were determined by the Grignard method as a measure of ion-exchange capacity. The surface hydroxyl site densities obtained were compared with the calculated value for the closest packing of hydroxyl groups, and the formation of hydroxyl groups was explained by neutralization of surface oxide ions by water. (Japanese)

Surface layers formed initially on copper in air containing water vapor and SO_2 as determined by IR-RAS and 2D-IR

J. Itoh, T. Sasaki, T. Ohtsuka and M. Osawa,

J. Electroanal. Chem., **473**, 256-264(1999)

To determine the components of corrosion products and the respective formation rates of the components, a series of in situ time-resolved IR-RAS spectra was measured on copper in air containing 8.7 ppm SO_2 and 80% relative humidity, and two-dimensional correlation analysis (2D-IR), which differentiates effectively overlapping bands and gives a clue to their band positions, was applied to the IR-RAS spectra. On the basis of the 2D-IR, deconvolution of the overlapping bands was carried out and the growth rates of the respective components of corrosion products were determined. The components of the surface layer formed in the environment are discriminated successfully by using 2D-IR and it is elucidated that sulfite and sulfate grow on the surface and Chevreul's salt ($CuSO_3Cu_2SO_3 \cdot 2H_2O$) is estimated as the main component of sulfite and $CuSO_4 \cdot 5H_2O$, that of sulfate. The formation of an adlayer of water appears preceding sulfite and sulfate, and the formation rate of sulfite is higher initially than that of sulfate, but the rate declines to become nearly equal to that of sulfate within experimental period. (English)

X-ray Diffraction Study of Carburization Transformation from Tantalum to Tantalum Carbide

Fumio Watari, Masaaki Takahashi and Keiji Yada

Proc.Int.Conf.Solid-Solid Phase Transformations '99(JIMIC-3), Kyoto, Ed. M.KOIWA, Jap.Inst.Met., p.317-320, 1999

The orientation relationship between Ta and TaC formed by carburization was determined by X-ray diffraction and the mechanism of transformation was considered. After the thin foil of Ta(011) single crystal was carburized by heating in benzene vapor and the products were identified by microdiffractometry, the single crystal X-ray diffraction experiments were done for the specimens before and after carburization. The Laue method showed that the product was TaC with the orientation relationship to the initial Ta matrix as Ta(011)[011]//TaC(112)[111]. Observation by optical microscopy and SEM showed that the striation was formed perpendicularly to TaC[111] direction on the surface of TaC. Both the orientation relationship between crystal structures and surface morphology of striae formation could be explained by the shear motion of TaC(111) atomic plane to the [112] direction which makes the stacking sequence of close packed planes change from bcc to fcc lattice.

Improvement of Chlorine Electrode in Al-Cl_2 Cell in NaCl-KCl Melt by Rotation

Mikito Ueda, Kohichi Imasawa, Shoichi Konda, Takeshi Sasaki, Tatsuo Ishikawa, and Toshiaki Ohtuka

Electrochemistry, **67**, 695-699 (1999)

To decrease the reaction polarization of the cathodic reaction of $Cl_2 + 2e \rightarrow 2Cl^-$ in Al-Cl_2 electrochemical cell in NaCl-KCl melt at 1023 K, we developed a cell system with a vertically rotating electrode composed of sliced graphite disks which are partially immersed in the melt. The apparent reaction resistance of the cathodic reaction was evaluated from transient potential and current changes of the cell. The reaction resistance decreases with an increase of the number of the graphite disks. The resistance is a function of the rotation rate of the electrode and exhibits the minimum value around a rotation rate of 20 rpm. The dependence on the rotation rate may be explained from Cl_2 concentration in a thin melt layer formed on the graphite electrode during exposure to Cl_2 gas phase. The rotation may introduce a continuous supply of the thin melt layer with a high concentration of Cl_2 to a reaction place at a meniscus part on the graphite electrode. However, if the rotation rate is too high, the exposure time of the thin melt layer to Cl_2 gas is not enough to establish an equilibrium concentration of Cl_2 in the layer. (English)

Recovery of Aluminum Alloy from Aluminum Dross by Treatment of Chloride-fluoride Mixture melt

Mikito Ueda, Mutsuhito Amemiya, Tatsuo Ishikawa, and Toshiaki Ohtsuka

J. Japan Inst. Metals, **63**, 279-283 (1999)

A new process for recovery of aluminum from aluminum dross was developed. The aluminum dross which is obtained as a by-product during casting process of aluminum alloy contains aluminum alloy and oxides of various metals including aluminum oxide. The process consists of two stages: (1) Separation of the aluminum alloy from the oxides by difference in density between the alloy and the oxide in molten salts. (2) Dissolution of oxides into molten salts, and electrolysis of the molten salts to form metallic aluminum from the oxide. This paper is concerned with the first stage for the separation of the aluminum alloy from the oxides by using $BaCl_2$-NaCl-NaF melts. The aluminum alloy completely separates from the oxides in the melts at concentrations of $BaCl_2$ higher than 33.3 mol%, in which the liquid aluminum alloy floats up and the oxides sink down. From a 30 g dross sample, amount of about 24 g of aluminum alloy has been recovered. The remaining oxides contain aluminum oxide, silicon oxide, magnesium oxide and iron oxide. From the aluminum oxide dissolved in the melt, metallic aluminum is formed by electrolysis in a subsequent stage. (Japanese)

Anti-Oxidation Property and Reaction Diffusion Process of Pre-Sulfidized TiAl Alloy

T. Yoshioka and T. Narita

Zairyo-to-kankyo, **48**, 90-95 (1999)

The oxidation resistance and degradation process were investigated in air at 1173K for up to 1.44 Ms for the TiAl alloy, which has been pre-sulfidized at 1173 K in a H_2-H_2S gas mixture to form a $TiAl_3$ (+$TiAl_2$) layer with 20 micron thickness on the alloy surface. And the reaction diffusion process of the $TiAl_3$-$TiAl_2$-TiAl system was computer-simulated.

The $TiAl_3$ layer with very good oxidation resistance changed quickly into a $TiAl_2$ at 80 ks, which agreed well with the calculated one. The $TiAl_2$ layer transformed slowly to a TiAl, indicating good oxidation resistance for up to 810 ks, while with further oxidation it degraded significantly at 1.44 Ms, in contrast to the calculated time of 4 Ms. This is due to a localized oxidation along alloy grain boundaries, and the degradation mechanism was proposed. (Japanese)

Effect of Al Content on the Internal Oxidation of Fe-Low Al Alloys at 1073 K

S. Hayashi and T. Narita

J. Japan Inst. Metals, **63**, 1204-1211 (1999)

Oxidation properties of Fe-3, 5, and 7mass%Al alloys were investigated at 1073 K in an oxygen gas atmosphere for up to 14.4 ks using thermo-gravimetry, scanning electron microscope, electron probe microanalyzer, and X-ray diffraction analysis. Time dependence of oxidation amounts can be divided into three regions, i.e., an initial stage with very high oxidation rate, a transient stage with a rapid decrease in the rate, and then a steady state oxidation. The critical times among these stages are 0.1 and 3.6 ks. The 7Al alloy oxidized very slowly, due to the formation of a duplex Al_2O_3 and Fe_2O_3 scale, in contrast to rapid oxidation of both 5Al and 3Al alloys. The 5Al alloy oxidized faster than the 3Al alloy during the initial stage, while for longer oxidation the 3Al alloy became faster. The 3Al alloy oxidized to form a thick scale with a triplex structure of Fe_2O_3, Fe_3O_4 and $FeAl_2O_4$, accompanied with an internal oxidation of duplex $FeAl_2O_4$ and Al_2O_3 zones. These internal oxides grew perpendicular to the alloy/scale interface. Oxidation of the 5Al alloy, close to the internal-external transition composition, is very complex depending on portions and oxidation times. It has a thin scale like the 7Al alloy and a thick scale with internal oxides like the 3Al alloy. Further, a precipitate free zone (PFZ) formed in the internal oxidation, sandwiched in between the $FeAl_2O_4$ and Al_2O_3 zones, and the formation mechanism of PFZ was proposed. (Japanese)

Effect of Nitrogen Gas on Oxidation properties of Fe-5mass%Al Alloy at 1073 K

S. Hayashi and T. Narita

Proc. of 14th ICC, Cape Town, South Africa, (1999)

Oxidation kinetics and scale structure of an Fe-5mass%Al alloy were investigated at 1073 K in various atmospheres: O_2, N_2-20vol%O_2, air, as well as in 5nine N_2 or Ar gases. Oxidation was rapid at the initial stage and then became slower, and the oxidation amounts at the initial oxidation stage decreased in the order: air, N_2-20vol%O_2, O_2, Ar, and N_2. When oxidized in an O_2 atmosphere, Al_2O_3, Fe_2O_3 and Fe_2O_3-nodules grew as surface scales, and Al_2O_3 precipitates in the alloy formed a network structure under the Fe_2O_3 scale. Oxidation in N_2-20vol%O_2 or air resulted in a surface scale of a duplex structure, with an outer scale of Fe_2O_3 and an inner thin scale of Al_2O_3 and Fe_2O_3. Further there was internal corrosion of Al_2O_3 precipitated perpendicular to the alloy surface and there was AlN in front of the internal oxidation. In the N_2 atmosphere Fe_2O_3 and Al_2O_3 formed a surface scale and internal corrosion due to impurity oxygen, but nitrides were not observed. The rapid oxidation observed in the initial reaction in N_2-20vol%O_2 and air appears to be due to the formation of Al_2O_3, Fe_2O_3, and AlN. The AlN further oxidized rapidly to Al_2O_3, leaving a relatively porous surface scale. Nitrogen gas penetrates into the alloy substrate, and with further oxidation the internal corrosion was divided into two zones, one an Al_2O_3 zone with rod-like precipitates and the other an AlN zone with a spike-like precipitates. (English)

Influence of Aluminum Content and Sulfur Partial Pressure on the Sulfidation Properties of Ti-Al Intermetallic Compounds

T. Yoshioka and T. Narita

Zairyo-to-kankyo, **48**, 214-219 (1999)

Sulfidation experiments of Ti-Al intermetallic compounds (Ti_3Al, TiAl, and $TiAl_3$) and pure titanium were carried out at 1073 K and 1173 K, and influence of aluminum content and sulfur partial pressure on the sulfidation amount was investigated. It was found that sulfidation amount decreases with increasing aluminum content. This is thought to be due to formation of Al_2S_3 in the scale and/or formation of the layer enriched with aluminum at the scale/alloy interface. It was shown that sulfidation amount decreases with decreasing of sulfur partial pressure. And then surface morphology changes from the fiber-like structure into the faceted structure with decreasing sulfur partial pressure. In the relatively low sulfur pressure and high aluminum content region, surface morphology shows fine granular or acicular structure. (Japanese)

Intergranular Corrosion Mechanism of SCH 13 Heat Resistant Steel in Waste Incineration Environment

H. Takahashi, Y. Miyakoshi, S. Kamota, S. Hayashi T. Narita, K. Kuroda, T. Saito and A. Kaji

Zairyo-to-kankyo, **48**, 583-587 (1999)

High temperature intergranular corrosion of a SCH 13 heat resistant steel in the waste incinerator, where plastics and used tires were burned under thermal cycling condition as at 1423 K after 6.2 ks and at 1150 K for 17 ks then cooled down to room temperature, was investigated by means of scanning electron microscope, electron probe micro-analysis and X-ray diffraction analysis. The network of intergranular corrosion within the alloy beneath the outer scale were identified. Si and Cr oxides as well as Cr and Mn sulfides were observed in the center of corroded area that was surrounded by Fe and Ni concentrated zone where Cr, Si, Mn were depleted.

The sulfur partial pressure calculated from composition of combustion gases was smaller than the dissolution pressure of sulfides of alloy element in SCH 13, it was supposed that Cr and Mn oxides that were near the surface and Cr, Mn sulfides that were at the inside of alloy were produced by a reaction between Cr. Mn and SO_2, O_2 gases.

At the initial stage of intergranular corrosion, Cr-Fe carbide channel that developed on grain boundary by repeated thermal cycle in waste incineration furnace was changed to oxide and then SiO_2 and voids were formed. Cr, Mn oxide and sulfide were formed by a reaction between Cr, Mn and SO_2, O_2 gases that were introduced by means of voids from gas side.

It is concluded that the Si, Cr, Mn depletion zone is caused by the formation of Si, Cr, Mn oxides and Cr, Mn sulfides, then Fe and Ni are relatively enriched on this depletion zone. (Japanese)

High-Temperature Oxidation Resistance of a Range of Intermetallics

Kazuya Kurokawa and Shigeji Taniguchi

Zairyo-to-Kankyo, **48**(3), 117-122 (1999)

Aluminides and silicides are receiving much attention as high-temperature structural materials having high oxidation resistance and consequently the oxidation resistance of these intermetallics has been investigated extensively. This review focuses on the oxidation behavior of Ni-aluminides, Ti-aluminides and Mo-silicides. The topics in Ni-aluminides are the time-depending change in the scale structure and the void formation at the scale/substrate interface. In Ti-aluminides, the modification of the scale structure by alloying additions and the effects of atmospheres on the oxidation behavior are described. The topic in Mo-silicides is the effects of defects and H_2O vapor on the accelerated oxidation. (Japanese)

Internal Oxidation and Nitridation Behavior of an Fe-5 mass% Al Alloy at 1073 K

S. Hayashi and T. Narita

J. Japan Inst. Metals, **63**, 1311-1316 (1999)

The internal oxidation and nitridation behavior of an Fe-5mass% Al alloy was investigated at 1073K in oxygen, nitrogen-20vol%oxygen(mix), and air atmospheres for up to 57.6 ks using thermo-gravimetry, scanning electron microscope, electron probe micro analyzer, and X-ray diffraction analysis. The time dependence of the amount of oxidation showed very high oxidation rate at the initial stage, a transient stage with a rapid rate decrease, and then steady state oxidation. The critical times between the transient and steady states were 900 s in air, and 2 ks in both the mix and in O_2. In the "steady state" condition, the oxidation rate in O_2 was very slow, while it was relatively faster in the mix and in air. In O_2, both a thin duplex (Fe_2O_3 and Al_2O_3) and a thick triplex (Fe_2O_3, Fe_3O_4, and $FeAl_2O_4$) scales formed and the film-like internal oxides grew beneath the thick triplex scale. In the mix and in air a thick scale formed with a triplex structure of Fe_2O_3, Fe_3O_4, and $FeAl_2O_4$ accompanied by an internal oxidation of duplex $FeAl_2O_4$ and Al_2O_3 zones, which grew perpendicularly to an alloy/scale interface, and spike-like AlN precipitates formed beneath the internal oxidation zone. Further, film-like Al_2O_3 formed locally at the top of internal AlN precipitates. A precipitate free zone (PFZ) formed between the internal oxidation and nitridation zone, and a formation mechanism for the PFZ was proposed. (Japanese)

Low Temperature Oxidation of Fully Dense and Porous $MoSi_2$

Kazuya Kurokawa, Hajime Houzumi, Isao Saeki, and Hideaki Takahashi

Materials Sci. and Eng., **A261**(Nos.1/2), 292-299 (1999)

The effects of pore and H_2O vapor on accelerated oxidation and pesting were observed from fully dense and porous $MoSi_2$ at 500°C in air and air-H_2O vapor atmospheres. Using fully dense $MoSi_2$ hindered occurrence of simultaneous oxidation of Mo and Si. In addition, H_2O vapor has no influence on the oxidation behavior of fully dense $MoSi_2$. On the other hand, porous $MoSi_2$ showed the accelerated oxidation behavior after an induction period. In the induction period, simultaneous oxidation occurred preferentially at pores and gradually spreaded over the surface. After this period, the mass gain increased linearly with a high rate due to generation and development of cracks, resulting in pesting. In porous $MoSi_2$, H_2O vapor in air accelerated the occurrence of pesting. This is probably due to the formations of metastable hydrates, $H_2Si_3O_7$ and $H_4Si_8O_{18}$, at pores. (English)

Oxidation Behavior of Fully Dense $MoSi_2$-SiC Composites Fabricated by In-Situ Synthesis

Kazuya Kurokawa, Makoto Ube, Jyunichi Kuchino, and Hideaki Takahashi

Proc. of 14th International Corrosion Congress, paper #75(CD-ROM), 1-8. (1999)

Oxidation behavior, especially at 773 K (the accelerated oxidation region), of fully dense $MoSi_2$-SiC composites fabricated by in-situ synthesis, was studied. The specimens were fabricated by two manners, viz., sintering of the mixed powders of elemental constituents, Mo, Si and C (in-situ synthesis) and the mixed powders of compounds, $MoSi_2$ and SiC. The results obtained in the present study are as follows: (1) fully dense $MoSi_2$-SiC composites can be fabricated by in-situ synthesis with a spark plasma sintering method. (2) In oxidation at 1773 K (passive oxidation region), the composites show outstanding oxidation resistance by a formation of a protective SiO_2 layer, regardless of SiC content and fabrication method. (3) The composites fabricated by in-situ synthesis show outstanding oxidation resistance even in the accelerated oxidation region. (4) The composites also show outstanding resistance to cyclic oxidation. (English)

Process of Scale Formation for the TiAl Alloy during High-Temperature Sulfidation

T. Yoshioka and T. Narita

Zairyo-to-kankyo, **48**, 220-225 (1999)

Sulfidation behavior of γ-TiAl alloy was investigated at 1173 K for up to 360 ks in H_2S-H_2 gas mixture. The process of scale formation was discussed from measurement of corrosion amount, observation of cross-sectional microstructure, identification of reaction products by X-ray diffraction and calculation of dissociation pressure of sulfides. The scale became duplex structure. In the outer scale, titanium sulfides (TiS, Ti_3S_4 ' TiS_2) and aluminum sulfide (Al_2S_3) were identified, while in the inner scale, titanium sulfides (TiS, Ti_3S_4) were identified. And the $TiAl_3$ phase was formed at scale/matrix interface. Corrosion rate changed at the test time of approximately 5.4 ks, and at same time, inner scale and $TiAl_3$ layer began to form. Titanium sulfide (TiS) was clarified to be more stable than aluminum sulfide (Al_2S_3) by calculation of dissociation pressure. From these results, the scale was considered to be formed in two steps. That is, the outer scale was formed during transient period, and then titanium was sulfidized alternatively, forming of the inner scale which mainly consists of titanium sulfide and the $TiAl_3$ occur during steady state. (Japanese)

The Effect of Si Concentration and Temperature on Initial Stage of High Temperature Oxidation of Fe-low Si Alloys

M. Fukumoto, S. Hayashi, S. Maeda and T. Narita

Tetsu-to-Hagane, **85**, 878-884 (1999)

Effect of Si and temperature on an initial stage of oxidation of Fe-Si (0-1.5 mass%) alloys in air was investigated for up to 150 s at temperatures between 1323 and 1473 K. Iron and the Fe-0.1%Si alloy formed a triplex oxide layer structure of FeO (Fe_3O_4 included)/Fe_3O_4/Fe_2O obeying a parabolic rate law and the temperature dependence of the parabolic rate constants yield activation energies of 101 and 156 kJ/m for Fe and an Fe-0.1%Si alloy, respectively. The alloys containing 1.0 and 1.5 Si showed very slow oxidation below 1373 K due to a formation of duplex Fe_2O_3 and SiO_2 layers. These alloys oxidized faster, obeying a linear rate law owing to liquid Fe_2SiO_4 formation in the triple layer structure of FeO (Fe_3O_4 included) /Fe_3O_4/Fe_2O_3 at 1473 K. At temperatures of 1373 and 1423 K the alloys containing 0.4, 0.5, and 1.0 oxidized slowly during initial periods and then the oxidation rate increased rapidly due to liquid Fe_2SiO_4 formation. Measurements of sample temperatures showed that this is due to over-heating of the sample by the rapid oxidation. The composite FeO and Fe_3O_4 layer between the FeO and Fe_30_4 layers was suppressed in the Fe and Fe-low Si alloys, when oxidized at temperatures below 1173 K, while it appeared even rapidly quenched samples oxidized above 1273K. (Japanese)

An agar-based silver / silver chloride reference electrode for use in micro-electrochemistry

Achim Walter Hassel, Koji Fushimi and Masahiro Seo

Electrochemistry Communications, **1**(5), 180-183 (1999)

A miniaturised Ag / AgCl reference electrode is described which can be easily set up. Its electrochemical behaviour was proven by micro-polarization curves, electrochemical impedance spectroscopy and potential transients. A saturated potassium chloride solution was used which was solidified by adding agar. The electrode is as small as 800 µm in diameter and 5 mm in length, with further potential for down-sizing. A modified version includes an agar salt bridge in the same capillary. After an induction period of 6 h the potential becomes stable within 1 mV for more than 6 weeks. The electrode shows a slightly different reference potential, which is discussed in terms of the production process. (English)

Anodizing of Aluminum Alloys

G.E. Thompson, H. Habazaki, K. Shimizu, M. Sakairi, P. Skeldon, X. Xhou and G. C. Wood

Aircraft Engineering and Aerospace Technology, **71**, 228-238 (1999)

Anodizing is used widely in the surface treatment of aluminum alloys for aeraspace applications. Considers recent advances in understanding of the influences of alloying elements in anodizing of aluminum alloys and, in particular, their applicability to second phase particles during anodizing of commercial alloys. Through more precise knowledge of the response of second phase materials to anodic polarization, improved anodizing and related surface treatment processes may be developed in order to enhance the performance of aluminum alloys. (English)

Anodizing of Aluminum Coated with Zirconium Oxide by a Sol-Gel Coating

Keiji WATANABE, Masatoshi SAKAIRI, Hideaki TAKAHASHI, Shinji HIRAI,
Sadae YAMAGUCHI

The Journal of the Surface Finishing Society of Japan, **50**, 359-366 (1999)

Aluminum specimens were covered with zirconium oxide film by a sol-gel coating and galvanostatically anodized in a neutral borate solution. The time variation in anode potential during anodizing was monitored, and TEM, EDX, RBS, and impedance measurement studied the structure and dielectric properties of the anodic oxide film.

We found that the anode potential increases with time, and that the slope of the potential-time curve increases with increasing the numbers of sol-gel dip coatings. During anodizing, an anodic oxide film, which consisted of an inner Al_2O_3 layer and an outer Al-Zr composite oxide layer, formed at the interface between Zr-oxide and the substrate, Fig. 1. The thickness of the inner layer increased with anodizing time, and the thickness of the outer layer peaked before decreasing with time. The capacitance of the specimen after sol-gel coating and anodizing was 20% higher than without sol-gel coating. The dielectric property of anodic oxide films was correlated with film structure.

The mechanism of anodic oxide-films growth on the specimen covered with Zr-oxide is discussed in terms of the porosity distribution in the Zr-oxide layer and the outward transport of Zr^{4+} ions across the composite oxide layer during anodizing. (Japanese)

Anodizing of Aluminum Coated with Zirconium Oxide by a Sol-Gel ProcessI. Effect of Heat Treatment on the Formation of the Anodic Oxide Film

Keiji Watanabe, Masatoshi Sakairi, Hideaki Takahashi, Katsumi Takahiro, Shinji Nagata and Shinji Hirai

Electrochemistry, **67**, 1243-1248(1998)

Aluminum specimens were covered with zirconium oxide films by sol-gel dip coating at T_h = 573 and 873 K, and then anodized in a neutral borate solution galvanostatically. The time-variation in anode potential during anodizing was monitored, and the structure of anodic oxide films was examined by TEM, EDX, and RBS.

During anodizing of specimens coated with ZrO_2 at T_h = 573 K, anode potential, E_a, increased linearly with time, t_a, and the slope of E_a vs. t_a curve increased with increasing the number of sol-gel coating. An anodic oxide film, which was composed of an inner Al_2O_3 layer and an outer Al-Zr composite oxide layer, grew at the interface between ZrO_2 layer and the metal substrate during anodizing. The thickness of the inner layer increased with t_a, whereas the thickness of the outer layer showed a maximum at a certain time before decreasing with ta.

Specimens coated with ZrO_2 at Th = 873 K showed 40 to 100 V-jumps in E_a at the very initial stage of anodizing, and then a slow increase in Ea. An anodic oxide film, which was composed of a single layer of Al_2O_3, formed beneath ZrO_2 layer during anodizing. Mechanism on the formation of anodic oxide films on aluminum coated with ZrO_2 films is discussed in terms of ion transport across anodic oxide films. (English)

Effect of Lanthanum Hydroxide Coatings on the High Temperature Oxidation of SUS430 Stainless steel

Akihiro Saito, Isao Saeki, and Ryusaburo Furuichi

Tetsu-to Hagane, **85**, 814-820 (1999)

Rare earth elements are effective for improving the oxidation resistance of stainless steels and chromia forming alloys at high temperatures. The reasons for the improvement, however, are not well understood and the effect of the content of rare earth elements is not clear. Most previous studies investigated high temperature oxidation of stainless steels and alloys containing rare earth elements where it is difficult to estimate the amount of rare-earth elements in the oxide.

In this study, type 430 stainless steel covered with a lanthanum hydroxide overlayer with various lanthanum contents was oxidized at 1373 K in a 1.671×10^4 Pa O_2 - 2.026×10^4 Pa H_2O - balanced N_2 atmosphere. It was found that the critical amount of lanthanum atoms, at which reduction of the oxidation rate becomes obvious, was about 10^{16} atoms cm^{-2}. This value is similar to published data obtained from studies of Fe-Cr alloys coated with different rare earth elements by surface coating or ion implantation. This may indicate that there is a critical limit for rare earth element effects to appear while other properties such as the morphology and oxidation number of the rare earth elements are secondary factors.

Observation of the oxide surfaces at the initial stages of oxidation showed that lanthanum oxide does not provide a physical barrier for oxidant migration through oxide films or provide preferential nucleation sites for Cr rich oxides. An explanation for the increased oxidation resistance with rare earth elements is a change in the growth mode of the oxide from a predominance of cation to anion diffusion. (Japanese)

Fabrication of Micro-Circuit Board via Anodizing Aluminum, Laser Irradiation and Electrodeposition

Tatsuya Kikuchi, Masatoshi Sakairi, Hideaki Takahashi, Yoshihiko Abe and Naoki Katayama

The Journal of the Surface Finishing Society of Japan, **50**, 829-835 (1999)

Fine-pattern coils were fabricated on an insulating board using anodizing, laser irradiation, nickel deposition, insulating board sticking, and aluminum substrate dissolution. Aluminum specimens covered with porous anodic oxide films were irradiated by a pulsed Nd-YAG laser through a beam splitter, iris diaphragm, convex lens, and quartz window in a nickel electroplating solution to remove anodic oxide film. During laser irradiation, the specimen was moved 3-dimensionally with an XYZ stage by a personal computer.

The width of the trench produced by film removal increased with increasing laser energy and with decreasing movement speed. After laser irradiation, nickel metal layer was electrodeposited at only the laser-irradiated area by cathodic polarization. The specimen stuck on epoxy resin before dissolving the aluminum substrate. Fine-pattern coils with nickel lines 15 μm wide and at 25 μm intervals were made on the insulating board. (Japanese)

Formation of Al-Zr composite oxide films on aluminum by sol-gel coating and anodizing

Keiji Watanabe, Masatoshi Sakairi, Hideaki Takahashi, Shinji Hirai, and Sadae Yamaguchi

Journal of Electroanalytical Chemistry, **473**, 250-255 (1999)

Al specimens were covered with zirconium oxide film by sol-gel coating using zirconium alkoxide, and then anodized galvanostatically in a neutral borate solution. The time-variation in anode potential during anodizing was followed, and TEM, EDX, RBS, and impedance measurements examined the structure and dielectric properties of the anodic oxide film.

It was found that the anode potential increases during anodizing, and that the slope of the potential-time curve becomes steeper with increasing number of dipping in sol-gel solution. An anodic oxide film was formed at the interface between zirconium oxide and the aluminum substrate during anodizing. This anodic oxide film was composed of an inner Al_2O_3 layer and an outer Al-Zr composite oxide layer. The capacitance of anodic oxide films formed after sol-gel Zr-oxide coating and anodizing was about 20% higher than without Zr-oxide coating. (English)

High Temperature Oxidation of Lanthanum Hydroxide Coated Type 430 Stainless Steel

Isao Saeki, Akihiro Saito, Ryusaburo Furuichi

Proc. 14th international corrosion congress, CD-ROM No.232 (1999)

Rare earth elements are effective for improving the oxidation resistance of stainless steels and chromia forming alloys at high temperatures. The reasons for the improvement, however, are not well understood and the effect of the content of rare earth elements is not clear. Most previous studies investigated high temperature oxidation of stainless steels and alloys containing rare earth elements where it is difficult to estimate the amount of rare-earth elements in the oxide.

In this study, type 430 stainless steel covered with a lanthanum hydroxide overlayer with various lanthanum contents was oxidized at 1373 K in a 1.671×10^4 Pa O_2 - 2.026×10^4 Pa H_2O - balanced N_2 atmosphere. It was found that the critical amount of lanthanum atoms, at which reduction of the oxidation rate becomes obvious, was about 10^{16} atoms cm^{-2}. This value is similar to published data obtained from studies of Fe-Cr alloys coated with different rare earth elements by surface coating or ion implantation. This may indicate that there is a critical limit for rare earth element effects to appear while other properties such as the morphology and oxidation number of the rare earth elements are secondary factors.

Observation of the oxide surfaces at the initial stages of oxidation showed that lanthanum oxide does not provide a physical barrier for oxidant migration through oxide films or provide preferential nucleation sites for Cr rich oxides. An explanation for the increased oxidation resistance with rare earth elements is a change in the growth mode of the oxide from a predominance of cation to anion diffusion. (English)

Local Deposition of Ni-P Alloy on Aluminum by Laser Irradiation and Electroless-plating

Songzhu CHU, Masatoshi SAKAIRI, Hideaki Takahashi, and Zhuxian QUI

Journal of The Electrochemical Society, **146**, 537-546 (1999)

A new technique on local modification of aluminum was attempted by combining aluminum anodizing, laser irradiation and electroless-plating. Aluminum specimen covered with porous anodic oxide film was immersed in Ni^{2+} / $H_2PO_2^-$ solution containing Pb^{2+} ions at $C_{Pb} = 0 - 1.8$ ppm, and irradiated with a pulsed YAG laser through lens and window to remove the oxide film locally at 293 K. The specimen was then transferred into the $Ni^{2+}/H_2PO_2^-$ solution at 358 - 368 K to examine the effect of C_{Pb} on the electroless Ni-P plating. Local deposition of amorphous Ni-P alloys (9-12 a/o P) only at irradiated area was obtained at $C_{Pb^{2+}} = 0.3 - 1.8$ ppm and above 363 K. The addition of Pb^{2+} to the solution caused the deposition of Ni-P with smooth surface and slightly affected the composition and structure of the deposits. (English)

Nucleation of Metals on Aluminum by Laser Irradiation and Effects of the Nuclei on Ni-P Electroless Deposition

S. Z. Chu, M. Sakairi, I. Saeki, and H. Takahashi

Journal of The Electrochemical Society, **146**, 2876-2885 (1999)

The mechanism of direct Ni-P electroless-deposition on aluminum by pulsed YAG laser irradiation in Ni^{2+} / $H_2PO_2^-$ solution has been investigated by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) with EDX analysis. Aluminum specimens covered with porous anodic oxide films were irradiated with a pulsed YAG laser in solutions containing Pd^{2+}, Cu^{2+}, Ni^{2+}, and Ni^{2+} / $H_2PO_2^-$ ions, and then localized electroless plating of Ni-P was attempted at the laser irradiated area.

It was found that laser irradiation in solutions containing Pd^{2+}, Cu^{2+}, or Ni^{2+} ions causes the deposition of small metallic particles of Pd, Cu, or Ni at the laser irradiated area on the aluminum surface, which was exposed to the solution after removal of anodic oxide film. The deposition of the metals is due to a redox reaction between the aluminum substrate and Pd^{2+}, Cu^{2+} or Ni^{2+} ions. By laser irradiation in Ni^{2+} / H:PO_2^- solution, Ni-P and Ni deposited by redox reactions between Ni^{2+} and $H_2PO_2^-$ as well as between Ni^{2+} and Al.

Pd and Ni-P and Ni particles deposited during laser irradiation acted as catalysts for the subsequent electroless Ni-P plating, while Cu particles exhibited no effect for it.
(English)

Effects of Sputter-Deposited Materials (W, Ti and SiC) on Interfacial Reaction between $MoSi_2$ and Nb

Kazuya Kurokawa, Genzo Ochiai, Hideaki Takahashi
Shigemasa Ohta, and Heishichiro Takahashi

Proc. of Intern. Symp. on Applied Plasma Sci., 2, p.337-342. 1999

In order to clarify effects of some sputter-deposited materials on the interfacial reaction between $MoSi_2$ and Nb, the diffusion couples of $MoSi_2$/Nb, $MoSi_2$/W/Nb, $MoSi_2$/Ti/Nb, and $MoSi_2$/SiC/Nb were annealed at 1673 K. The structure and growth rate of the reaction layer and the reaction path were investigated. The growth of reaction layer was mainly dominated by the diffusion of Si toward the Nb side to form the principle structure consisting of $MoSi_2$//(Mo, Nb)$_5$Si$_3$/Nb5Si3//Nb and followed a parabolic rate law. W-coating accelerated the interdiffusion of Mo, Nb and Si through the reaction layer, whereas Ti-coating and SiC coating suppressed the interdiffusion. (English)

Fabrication of $MoSi_2$-SiC Compocsites by a Spark Plasma Sintering Method

K. Kurokawa, M. Ube and H. Takahashi

Journal of Univ. of Sci. and Tech. Beijing, **6**(2), 116-118 (1999)

Fully dense $MoSi_2$-SiC composites were fabricated from the mixed powders of the elemental constituents by a spark plasma sintering (SPS) method. Sintering and densification of the Mo-Si-C mixed powders are accomplished through three processes. In particular, they proceed rapidly by the formation of $MoSi_2$. The most suitable temperature for the fabrication of $MoSi_2$-SiC composites depends on the content of SiC and increases with increasing SiC content. As a result, fully dense $MoSi_2$-SiC composites can be prepared without difficulty by a spark plasma sintering method. (English)

NiAl Coating of Carbon Steel by Reactive Sintering

K. Matsuura, K. Ohsasa, N. Sueoka and M. Kudoh

Materials Science Forum, 308-311, 244-249 (1999)

In order to investigate the feasibility of the synthesis of NiAl and simultaneous NiAl coating of an ultra-low carbon steel, a mixture of nickel and aluminum powders are sintered at 1473 K on the surface of the steel at a pseudo-isostatic pressure of 150 Mpa. It is shown that the synthesis of dense nickel monoaluminide, NiAl, is completed and simultaneous NiAl coating of the steel are successful. There are no defects such as cracks or cavities in the synthesized NiAl even at the bonding interface. The thickness of the NiAl coating is approximately 800 µm. Iron diffuses into the NiAl, while nickel and aluminum diffuse into the steel. The diffusion distances are 50, 200 and 300 µm for iron, nickel and aluminum, respectively. Vickers microhardness changes continuously from 330 in the NiAl to 80 in the steel. (English)

Nickel Monoaluminide Coating on Ultralow-Carbon Steel by Reactive Sintering

K. Matsuura, K. Ohsasa, N. Sueoka and M. Kudoh

Met. Mater. Trans.A, **30A**, 1605-1612 (1999)

By sintering a mixture of nickel and aluminum powders on the surface of an ultralow-carbon steel block of 15 mm in thickness, nickel monoaluminide (NiAl) is reaction-synthesized and simultaneously joined to the steel block. When the thickness of the compact powder mixture is above 5 mm, an exothermic, self-propagating high-temperature reaction of Ni + Al → NiAl is induced by heating to approximately 900 K, and the temperature of the compact rises very quickly and exceeds the melting point of NiAl (1911 K). Accordingly, an in situ NiAl coating on the steel is completed in a very short time. When the compact thickness is below 5 mm, on the other hand, the synthesis reaction is incomplete because of heat loss due to absorption by the steel block, and intermediate products such as Ni_3Al and $NiAl_3$ remain in the compact. However, the in situ coating is completed by further heating to 1473 K followed by holding for 0.54 ks. Across the interface between the steel and the coating, the concentrations of the elements gradually change and, accordingly, the Vickers hardness continuously changes from approximately 80 in the steel to 350 in the NiAl. The joint strength evaluated from a tensile test is above 150 MPa. (English)

Numerical Modeling of the Transient Liquid Phase Bonding Process of Ni using Ni-B-Cr Ternary Filler Metal

K. Ohsasa, T. Shinmura and T. Narita

J. Phase Equilibria, **20**, 199-214 (1999)

A modeling of dissolution and isothermal solidification during the transient liquid phase (TLP) bonding process of nickel using Ni-15.2mass%Cr-4.0mass%B ternary filler metal was carried out by combining thermodynamic calculation with ThermoCalc software and diffusion analysis by a finite difference method. In the modeling, diffusion-controlled transformation was assumed, and the equilibrium compositions at the solid-liquid interface were calculated using ThermoCalc software. The interface velocity was determined from the mass balance of solutes diffusing into or out from the interface. When the Ni specimen with a filler metal of 30 μm in thickness was kept at 1473 K for 3.6 ks, isothermal solidification was almost completed in the analysis. On the other hand, when the specimen was kept at 1373 K for 3.6 ks, residual liquid remained at the bonding region. The solidification sequence of the residual liquid during the cooling stage was calculated by the Scheil simulation. The simulation showed that solidification of the residual liquid is completed with a ternary eutectic reaction, $L \rightarrow fcc+Ni_3B+CrB$. The calculated width of the eutectic region agreed well with the experimental result. (English)

Probabilistic Simulation of Grain Structure Formation in Casting

K. Ohsasa

Proc. of Intern. Symp. on Computer Simulation of Solidification and Casting,
Osaka, Japan, 61-68 (1999)

A probabilistic algorithm for simulation of grain structure formation during the solidification of an alloy casting based on a Monte Carlo method is proposed. Nucleation and grain growth of crystals in the casting is controlled by a probabilistic function that determines the probability of nucleation and grain growth according to the degree of supercooling of alloy melt. Heat transfer and diffusion calculations were coupled with the Monte Carlo procedure to take into account the effects of temperature and solute fields on nucleation and grain growth. The latent heat evolution and solute rejection due to nucleation and grain growth produced by the Monte Carlo procedure were fed back to the heat transfer and diffusion calculations. Crystal relocation due to pouring flow was introduced, and this brought about crystal multiplication, known as a 'big bang'. The effect of gravity on grain structure was considered by moving suspended crystals to downward according to the Stokes equation. Aluminum-silicon alloys were used in the simulation, and the influences of process variables such as the superheat of melt and initial silicon content on the grain structure were examined. In order to confirm the validity of the model, experimentally obtained structures of castings were compared with those obtained from the simulation, and the tendencies found in the calculated results agreed well with those in the experimental results. (English)

Carbonization of Boron Containing Polyimide Films - B-N Bond Formation -

H. Konno, H. Oka, K. Shiba, H. Tachikawa and M. Inagaki

Carbon, **37**, 887-895 (1999)

Two types of boron containing polyimide (Kapton type) film were prepared either by adding dihydroxyphenylborane (DPB) to polyamic acid [mixing method] or by using diaminodiphenyl ether having a boron containing functional group (DDE-B) to prepare polyamic acid [substitution method]. Formed polyimide films containing boron were carbonized at 600-1200°C. By doping boron into the precursor polyimide, preferential formation of B-N bonds in carbonized films was observed and appreciable amounts of nitrogen were chemically trapped in the carbon film even after carbonization at 1200°C. The polyimide prepared by the substitution method gave uniform carbon films in composition and structure, though DDE-B is not simply synthesized and didn't polymerize to high degree. The polyimide prepared by the mixing method gave non-uniform carbon films, but the process was very simple and possible to increase boron content by using different boron compounds. (English)

Effect of Oxygen Plasma Treatment on Gas Adsorption Behavior and Surface Structure of Carbon Spheres Derived from Phenol Resin

M. Inagaki, M. Sunahara, A. Shindo, V. Vignal, H. Konno

J. Mater. Res., **14**, 3208-3210 (1999)

Plasma treatment was applied on glasslike carbon spheres to modify their gas adsorption behavior. After the oxygen plasma treatment, a selective adsorption of CO_2 gas was obtained, almost no nitrogen adsorption being detected, at low temperatures.Surface morphology observed by using field-emission scanning electron microscopy, atomic force microscopy, and scanning tunneling microscopy was found to be changed after the oxygen plasma treatment. (English)

Effects of Carbonization Atmosphere and Subsequent Oxidation on Pore Structure of Carbon Spheres Observed by Scanning Tunneling Microscopy

M. Inagaki, V. Vignal, H. Konno, A. W. Morawski

J. Mater. Res., **14**, 3152-3157 (1999)

The surface of carbon spheres was studied by using field-emission scanning electron microscopy and scanning tunneling microscopy paying particular attention to the effects of atmosphere during carbonization and of subsequent oxidation on shape and size of the entrance of micropores. Commercial spheres of glasslike carbon prepared by carbonization of phenol resin spheres in ether N_2 or CO_2 atmosphere were subjected to the oxidation by immersing into nitric acid and then heating in air at 400°C. The size distribution of pore entrance at nanoscopic scale was determined from scanning tunneling microscope images. Carbon spheres prepared in CO_2 atmosphere had predominantly ultramicropores, but those prepared in N_2 had a very low porosity. The behavior during the oxidation process in air was found to be quite different on these two carbon spheres; spheres carbonized in N_2 were oxidized heterogeneously, but those in CO_2 showed homogeneous oxidation, giving a high density of ultramicropores. (English)

Electrodeposition of Mixed Valence Molybdenum Oxyhydroxide Films and Their Characterization

H. Konno, T. Ito, M. Otani and K. Sasaki

J. Metal Finish. Soc. Jpn., **50**, 909-914 (1999)

Dark brown oxyhydroxide films were formed on aluminum, copper, and ITO glass by cathodic pulse electrolysis in a 0.016 mol L^{-1} $(NH_4)_6Mo_7O_{24}$-0.32 mol L^{-1} $MgSO_4$ solution of pH 5 at 50°C. The XPS and ICP-AES analyses indicated that the films were composed of mixed valence molybdenum ions of Mo(IV) to Mo(VI), Mg(II) ions, and small amounts of sulfate ions. The $MgSO_4$ is a necessary component in the solution to obtain uniform and adhesive films. The NH_4^+, Na^+ or Zn(II) ions substituted for Mg(II) ions, and acetate, nitrate or phosphate ions substituted for sulfate ions in the solution adversely affected the formation of uniform and adhesive films. Though the decrease of Mg(II) ions in the solution increased the amount of Mo ions in the film, it also showed adverse effects. The films were amorphous by XRD even after drying at 200°C for 12 h. Diffuse reflectance spectra of films showed that transmittance is about 15% in the UV-VIS region of 200-700 nm in wavelength and increases to 70-80% in the near IR region of 1.5-2 μm. Spectrophotometric emissivity measurements at 100°C indicated that emissivity in the IR region of 4-10 μm is around 40% and increases drastically to over 90% for wave length longer than 10 mm. It indicates that the film is a selective emitter/absorber for far the IR region. The film also showed electric conductivity. (Japanese)

Nitrogen Incorporation into Boron-Doped Graphite and Formation of B-N Bonding

H. Konno, T. Nakahashi, M. Inagaki and T. Sogabe

Carbon, **37**, 471-475 (1999)

Carbon materials having different levels of boron doping was prepared from the mixture of coke and boron carbide at temperatures between 2000-2800 °C. The XRD measurements showed that crystallites grow with the increase of boron concentration during the preparation and there is a limited concentration of boron in solid solution. Unexpectedly, XPS measurements revealed the increase of N 1s peak intensity with the increase of B 1s peak intensity. The binding energies of these peaks suggested the formation of B-N type bond, though it was not observed by XRD. It implies that the doped boron gives rise to the incorporation of nitrogen in the surface layer of carbon materials. Possible source of nitrogen is air occluded in raw materials during packing into graphite crucibles. Such small amounts of nitrogen must be taken into account with boron doped carbon materials at high temperatures. (English)

Preparation of Carbon-Coated Transition Metal Particles from Mixtures of Metal Oxide and Polyvinylchloride

M. Inagaki, Y. Okada, H. Miura, H. Konno

Carbon, **37**, 29-334 (1999)

Carbon-coated α-iron particles ca. 100 μm in diameter were prepared through a simple heat-treatment of mixtures of Fe_3O_4 and polyvinylchloride (PVC) at 1000°C in an Ar flow. After HCl treatment of the particles to remove iron and iron compounds, hollow carbon particles were seen under the scanning electron microscope. According to thermogravimetric analysis of the Fe_3O_4-PVC mixture, the formation of carbon-coated α-iron particles proceeds in four steps with weight loss, the first two steps being due to the pyrolysis and carbonization of PVC, and the last two to the reduction of Fe_3O_4 to α-Fe. Using the other transition metal oxides, NiO, CoO and Cu_2O, carbon-coated respective metal particles were also prepared using the same procedure. (English)

Quantitative Assessment of Pores in Oxidized Carbon Spheres Using Scanning Tunneling Microscopy

V. Vignal, A. W. Morawski, H. Konno, M. Inagaki

J. Mater. Res., **14**, 1102-1112 (1999)

Surface heterogeneity, particularly shape and size of pores on the surface of activated carbon spheres were studied by using scanning tunneling microscopy (STM) and field-emission type scanning electron microscopy (FE-SEM). Spheres were carbonized either in N_2 or CO_2 atmosphere and oxidized ones were used as samples. A new numerical method based on the determination of contour maps from STM images was proposed in order to determine the size distribution in micropores. These results were discussed with respect to the adsorption of gas and liquid molecules. A good correlation between Brunaner , Emmett, and Teller (BET) surface area determined from adsorption isotherms of N_2 at 77 K and the number of pores with the size of 0.5-1.8 nm was observed, indicating that the proposed procedure to analyze the pore size distribution is effective. (English)

Structural Defects Created on Natural Graphite Surface by Slight Treatment of Oxygen Plasma – STM observations –

E. Bourelle, H. Konno, M. Inagaki

Carbon, **37**, 2041–2048 (1999)

The creation of structural defects on natural graphite surfaces by slight treatment of oxygen plasma was studied by scanning tunneling microscopy (STM) at nanoscopic scale. Most of the defects were vacancies with the depth of one or two layers, while the mean number of defects per μm^2 of graphite surface and the mean area of defects increased with the increase in input power, time and temperature of the irradiation. After very slight treatment at room temperature, single carbon atom vacancies were obtained on graphite surfaces with a percentage more than 50%, though some large vacancies were formed. After slight irradiation at a high temperature (400°C), an agglomeration of defects occurred (the mean area increases whereas the defect density decreases), while the defects once formed were difficult to be annealed by heating at high temperatures up to 400°C in vacuum. The present work showed the possibility to control the modification of natural graphite surfaces for further application by changing the condition of oxygen plasma treatment. (English)

Superstructure and Boundary Structure in Stage 4 $MoCl_5$-Graphite Intercalation Compounds Studied by Atomic Force Microscopy and Scanning Tunneling Microscopy

V. Vignal, H. Konno, M. Inagaki, S. Flandrois, J. C. Roux

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Intercalated domains on stage 4 $MoCl_5$-graphite intercalation compounds ($MoCl_5$-GIC's) were observed by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). On large intercalated domains, a superstructure was found, in relation with a modulation of the electronic properties of the first layer of carbon. From that, the structure of the chloride ions layer was discussed and a model including dimer molecules was proposed. At the boundaries between large intercalated and nonintercalated domains, corrugations were observed along certain crystallographic directions of graphite. Their morphology was studied in detail at atomic scale and formation mechanisms were proposed. Small intercalated domains were also observed. Their shapes were irregular but their boundaries were clear cut. (English)

Suppression of Microbially Mediated Dissolution of Pyrite by Natural Organic Acids in Acidic Environments

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Natural organic acids, such as tannic acids (TA), wood vinegar (WV), fulvic acids (FA), and humic acids (HA), were investigated as suppressants of microbially mediated dissolution of pyrite with *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* in acidic media at pH 2-4, and the suppression mechanism is discussed. The suppression occurs by adsorption of natural organic acids on pyrite, inhibition of cell growth, as well as reduction and complexation of Fe(III) ions. Most of these factors are affected by pH: the suppression by FA was stronger at pH 2 than at pH 3-4, because the affinity between pyrite and the aromatic groups in FA is stronger blow the isoelectric point (*iep*) of pyrite (around pH 2.5). Cell growth was more strongly inhibited by natural organic acids at lower pH.

The order of suppression was WV>TA>>FA>HA at all pHs here, and dependent on the number of functional groups, such as phenolic and carboxylic groups in the natural organic acids. The pK_a of WV was 5.0, and the acid-base titration and elemental analysis suggested that WV contains acetic acid and large amounts of other organic acids. Wood vinegar was found to suppress and retard pyrite dissolution over a wide pH. (English)

Synthesis, Structure and Stability of $MoCl_5$–Graphite Intercalation Compounds

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The mechanism for the synthesis of $MoCl_5$-graphite intercalation compounds ($MoCl_5$-GICs) with stage-1 structure, which was successfully done in the presence of either $MoOCl_3$ or MoO_3 with $MoCl_5$, was discussed. The formation of reactive chlorine gas was supposed to be important for the formation of stage-1 structure. Well-ordered stage structures along the *c*-axis were easily obtained in $MoCl_5$-GICs synthesized from natural graphite and also from highly-crystallized graphite films. From detailed observation by STM/AFM on stage-4 GICs, a superstructure in the graphite basal plane (in-plane structure) was found in large intercalated domains with an area of more than 150 μm^2, having a hexagonal symmetry of which axes rotated by about 30° from graphite axes and having a periodicity of 1.9 nm. The boundaries between large intercalated and non-intercalated domains consisted of liner segments which were parallel to certain crystallographic axes of graphite, but those between small intercalated domains with the area less than 100 nm^2 and non-intercalated domains were irregular. These $MoCl_5$-GICs were experimentally shown to have very high stability in various liquids, all of which can dissolve $MoCl_5$ itself. Even in boiling water, the compounds prepared from graphite hosts with a flake size as 400 μm showed only a trace of decomposition of GICs, but those from a flake size as small as 10 μm were decomposed. (English)

Biocompatibility and bioreactivity of Ti-based functionally graded implant

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The metal-ceramics and metal-metal composites with functionally graded structure(FGM) were made and the biocompatibility with hard and soft tissue was evaluated by animal implantation tests. The metal/ceramics implant with the miniature size 2 × 10 mm was composed of titanium(Ti) at one end, increasing the content of hydroxyapatite(HAP) to the other end. The surface and cross section were observed by SEM and EPMA elemental mapping and the FGM structure was confirmed. The new bone formation around the Ti/20%HAP FGM implants inserted in femora of rats was observed by the conventional method using the optical microscope and by imaging using the reflected electrons in SEM and the EPMA elemental mapping method. The implant showed the good biocompatibility and there was little difference in new bone formation between Ti and HAP rich region. The tissue reaction to Ti/100%Co FGM implant inserted in subcutaneous tissue was also observed. As the concentration of Co increased along the longitudinal direction of implant, the surrounding tissue became more inflammatory. These showed that the tissue reaction changes gradiently in response to the change of biocompatibility formed by the gradient structure of FGM.

Biocompatibility of Refractory Metals in Group IVa and Va Evaluated by Bioimaging Methods

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To evaluate the biocompatibility of refractory metals in group IVa and Va, these metals were implanted in rats, then subjected to metal surface roughness test by atomic force microscopy, histological examination by optical microscopy, histomorphometry by image analyzer, mapping of metal dissolution by X-ray scanning analytical microscopy and EPMA, observation of osteogenesis by confocal laser scanning microscopy (CLSM) and highly sensitive analysis by ICP. None of metals except vanadium showed any inflammatory response. The amount of new bone changed little and the bone-metal contact increased markedly from the 2nd to 4th week after implantation. The image of fluorescent labeling by CLSM and calcium enrichment by EPMA revealed that remodeling and calcification proceeded. While vanadium showed a suppressive effect in bone formation. ICP showed vanadium dissolved after immersion in simulated body fluid.

These results suggest that zirconium, hafnium, niobium and tantalum have good biocompatibility equivalent to that of titanium.

Biocompatibility of Titanium/Hydroxyapatite and Titanium/Cobalt Functionally Graded Implants

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Zurich, p.356-361, 1999

To investigate the tissue reaction to the gradient composition of FGM implant the animal experiments were done comparatively for titanium/hydroxyapatite(Ti/HAP) and titanium/cobalt(Ti/Co) FGM implants as well as the pure metal implants. FGM implants were prepared by powder metallurgical method through the process of either gradiently packing dry powders into mould or gradiently distributed by sedimentation inside solvent liquid followed by compressing and sintering. Pure Ti, Ti/20%HAP and Ti/100%Co were implanted in hard tissue and soft tissue of rats and rabbits. Tissue response and osteogenesis after implantation were evaluated from histological observation by optical microscopy using the thinly sectioned, stained specimens and from elemental mapping by EPMA and XSAM(X-ray scanning analytical microscope) using the unstained block specimens. Implantation test of Ti/20HAP into hard tissue showed very little difference in new bone formation for pure Ti region and HAP-rich region. This is mainly because both Ti and HAP have good biocompatibility. In the implantation test of Ti/Co into soft tissue the thin fibrous tissue was formed in pure Ti region. The tissue layer thickness was increased with Co concentration, forming the more inflammatory tissue in Co rich region. The change of concentration of Co seemed to affect on the biocompatibility of implant material. The tissue reacted gradiently in response to the gradient composition of FGM implant. This implies the possibility to control the tissue response through the gradient function of FGM.

Dissolution of nickel and tissue response observed by X-ray scanning analytical microscopy

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The recently developed scanning X-ray analytical microscope (XSAM) was applied for the analysis of the soft tissue of rat in which Ni was implanted and serious inflammation occurred, to investigate the relationship between tissue response and elemental distributions. The XSAM observation was carried in air without pretreatment and staining of samples. Mapping images of P, S, Ca, Fe and Ni, which were the elements with low concentration in soft tissue, were obtained from the soft tissue blocks of rat where Ni was implanted. S mapping image showed the localization of S in muscle and in hairs. Ca mapping image showed the localization of Ca in muscle and hair roots. Fe distribution was also observed and the localized area was consistent with the hemorrhagic area. The Ni dissolution area was clearly detected around the Ni implant. The comparison with the histological observation showed that the Ni dispersed area was consistent with the inflammatory area and the degree of tissue damage was closely related to the dissolved Ni concentration.

Effects of water immersion on mechanical properties of new esthetic orthodontic wire

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American Journal of Orthodontics and Dentofacial Orthopedics, **116**(5), 533-538 (1999)

New fiber-reinforced plastic orthodontic wire (FRP wire) was fabricated with polymethyl methacrylate (PMMA) for matrix and biocompatible $CaO-P_2O_5-SiO_2-Al_2O_3$ (CPSA) glass fibers for fibers that have not only high esthetics but also mechanical properties similar to those of metal wires. The purpose of this study was to evaluate the effects of water immersion on the mechanical properties of this new wire. The FRP wire specimens were 0.5 mm in diameter with 29.1-60.4% volume fraction of fibers that were 20μm in diameter. A three-point flexural test was performed to obtain the elastic modulus (E) and flexural load (P) at the deflection of 1 mm under dry and wet conditions. Stress relaxation of the wires was tested under dry and wet conditions, and the wire diameters were measured before and at 20 days after immersion. The results showed that there were changes in E up until 10 days and in P up until 20 days after immersion. The values of E and P at 30 days after immersion were 93% and 87%, respectively, of those before immersion. Stress relaxation occurred rapidly from the start of immersion until about 60 min under dry conditions and about 120 min under wet conditions and then approached saturation. The swelling of hydrated FRP wires affected the wire diameter, although this effect was not significant. The results of this study therefore suggest that the mechanical properties of FRP wires are reduced by water immersion in the initial stage.

Fabrication of Aesthetic Orthodontic Wires with Flexural and Torsional Stiffness by Photo Curing Method

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To realize aesthetic orthodontic wires, we have been developing the FRP wires in combination with biocompatible $CaO-P_2O_5-SiO2-Al_2O_3$(CPSA) glass fibers and PMMA matrix by a hot drawing method. These wires are mainly intended to be used for the movement of teeth during the initial stage of treatment. In this study, a photo cure polymerization method was applied to form the rectangular timber with a sufficient torque force for rotation of the teeth. The FRP wire composed of CPSA glass fibers and UDMA matrix showed a sufficient flexural strength. For torsional properties, however, the wire had a much smaller torque compared with that of Co-Cr and Ni-Ti wires. The FRP using dental composite resin for matrix showed a load 4 times of UDMA based FRP wires. The torsional load was increased to 1/2 of Ni-Ti wire. It was found that the fiber content mainly contributes to flexural load while the use of stiff materials such as composite resin for the matrix is much more effective for improving torsional properties.

Firing Shrinkage of Porcelain-resin Composites Prepared by Laser Lithography Machine

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Dental Materials Journal, **18**, 444-452 (1999)

Using porcelain and resin-mixed composites as experimental materials, cubic polymerized composites were made by the accumulation of thin slices cured by laser scanning. The composites were then fired, and bulk ceramic bodies were made. The optimal firing conditions of polymerized composites and firing shrinkage were investigated. The results showed that cubic ceramic bodies in a form homologous to that before firing could be reproduced. The volume shrinkage of fired ceramic bodies consisting of 1 g of ceramic powders and 0.3 g of epoxy resin was about 30% under all firing conditions, and there were no significant differences between specimens. It was suggested that with further research and development, three-dimensional forms for clinical use in dentistry could be manufactured by the proposed method.

Temperature-dependence of the mechanical properties of FRP orthodontic wire

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Dental Material Journal, **18**(2), 167-175 (1999)

The temperature-dependence of the mechanical properties of a new esthetic orthodontic wire with fiber-reinforced plastic (FRP) structure was investigated. The new FRP wire, fabricated by a hot drawing method, is 0.5 mm in diameter and has a multiple fiber structure composed of biocompatible CaO-P_2O_5-SiO_2-Al_2O_3 glass fibers of 20 µm in diameter and a polymethyl methacrylate matrix. The flexural load at a deflection of 1 mm and Young's modulus at 24, 37, and 50°C under wet conditions showed similar fiber fraction dependence to those under dry conditions for a fiber fraction of 40-51%. The flexural load and Young's modulus tended to decrease slightly with increases in temperature. This tendency was larger for the lower fiber fraction. However, the difference in flexural load for a temperature difference of between 24°C and 50°C was at most 10 gf. This is negligibly small, and a constant orthodontic force regarding temperature change would be advantageous from a clinical point of view.