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CURRENT ACTIVITIES and PRESENTATIONS

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Our research activities are concerned with corrosion and corrosion prevention of metals and molten salts electrolysis.

Research programs in progress are as follows:

(1) New corrosion resistive films consisting of conductive polymers

A conductive polymer coating was applied to corrosion prevention of carbon steels. A bilayered polypyrrole (PPy) film doped by molybophosphate (MoP) ions at the inner layer and by organic ions at the outer layer was electrochemically formed on the steel plate in aqueous solution containing pyrrole monomer. The corrosion protection of the layer was tested by immersion of the PPy-coated steel in aqueous 3.5 % NaCl solution. The passivity of the steel was maintained for time period longer than 100 h, where appreciable corrosion was not observed. The self-healing property of the coated steel was also examined.

(2) Monitoring of corrosion products on model cut-edge of zinc alloy coated steels by Raman spectroscopy

Corrosion products on zinc layer coupled with bare steel in atmosphere were studied by Raman spectroscopy under the in-situ and ex-situ condition. At the presence of NaCl precipitate, zinc-hydroxy carbonate was observed on the bare surface, while zinc-hydroxy chloride was detected. The difference of the corrosion products was explained by pH values of the sites. The bare steel site works as a cathode and the solution of the absorbed thin layer shifts to more alkaline and the zinc-coated site as an anode and the solution remains slightly acidic solution. The precipitation to zinc-hydroxy carbonate or zinc-hydroxy chloride, which was estimated from the equilibrium calculation under a constant Cl^- concentration, was found to be dependent on the pH value of the solution. The effect on the corrosion products of the amount of the NaCl precipitate and humidity in atmosphere was examined.

(3) Corrosion of Pt-Co and Pd-Co alloy electrode for application of PEFC cathode

As the cathode of PEFC with high performance for the oxygen reduction reaction (ORR), alloying of Co into Pt or Pd was proposed. The corrosion of the alloys was survayed by ICP-AES, in which the amounts of Co and Pt or Pd dissolved during potential scans of a thousand cycles between the hydrogen and oxygen regions was measured. For the Pt-Co alloys the corrosion was not appreciable at the Co addition less than 50 mol%. The Pd-Co alloys are more corrosive.

(4) Electrodeposition of Al-Zn alloys in chloride molten salt

Al-Zn-X(X=Cr, Mn) alloys were electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $ZnCl_2$ and $CrCl_2$ or $MnCl_2$ for corrosion protection of steel. The electrodeposition was performed by constant potential electrolysis or potential pulse electrolysis. The Zn content in the alloy gradually increases from 2 to 95 at% at potential from -50 to 100 mV (vs. Al/Al(III)). The Cr content increases from 0 to 10 at% at the same potential region. The surface morphology of the deposit was improved by Cr content compare with it of Al-Zn alloy.

(5) Electrodeposition of Bi-Sb-Te alloy in chloride molten salt

Bi-Sb-Te alloys were electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $BiCl_3$, $SbCl_3$, and $TeCl_4$ at 423K. Stable deposition of pure Bi and pure Te were not obtained by the electrolysis, because electrodeposited Bi and Te dissolved into the molten salt immediately. The composition of Bi-Sb-Te depended on concentration of Sb ion in electrolyte between 5 and 9 mM. The thin film of $Bi_{0.5}Sb_{1.5}Te_3$ which is thought to be one of the best thermoelectric conversion device was obtained on glassy carbon electrode by pulse potential electrolysis.

(6) Development of functional glass by ion-exchange reaction in molten salt

Glass plates were immersed in a molten salt of $NaNO_3$-$TlNO_3$ at 673-723 K. During the immersion, ion-exchange was induced at the surface of the glass. By the reduction of the glass, Tl ion changed to metallic Tl and then the glass exhibited strong light absorption in visible light from 400 to 700 nm wavelength.

(7) Photoluminescence from passive films of Ni by UV-light excitation

Luminescence light from the anodic thin oxide films formed on Ni in acidic H_2SO_4-Na_2SO_4 solution (pH=2.3) was measured by UV-light irradiation with 3.82 eV energy. The peak wavelength of the luminescence light from the film shows about 410 nm. The wavelength corresponds with the energy at 3.0eV of band gap of NiO.

(8) Electrorefining of Na for recycling of used Na-S secondary batteries

To develop electrorefining process of metallic Na from the used Na-S battery. There is no electrorefining process of sodium in the industrial scale. We investigated electrolytic melts for the process and was selected propylene carbonate as a candidate of the electrolytic melt. In the electrorefining experiment, 99.9% pure Na was obtained from simulated Na in used Na-S battery.

(9) Characterization of Rust Layer on Weathering Steels

The Rusts formed on weathering steel exposed in various sites in Japan for 17 or 18 years and on the Ni-containing steel exposed for 1-3 years were studied. The absorption of water vapor into the rust was measured by in-situ gravimetry. 8-10 % volume ratio of water was absorbed in the rust layer. The impedance and near IR (NIR) reflectance were also measured during the water absorption. The impedance is decreased with adsorption/ absorption of water vapor. The water molecules adsorbed/ absorbed make electric channels in the rust and further induces a change from the insulating rust to slightly conducting rust due to a reduction of Fe(III) to

Fe(II). Combination bands of water were observed on the NIR reflection spectra,

Other Activities

Prof. Ohtsuka attended the International mini-Symposium on Control and Analysis of Reactions on Electrode/Solution Interface in Atomic/Molecular Resolution, Sapporo, Hokkaido University, March 10, 2008 and presents three papers. He also attended Pacific Rim Meeting on Electrochemistry and Solid-state Science (PRIME), Honolulu-Hawaii, Oct., 12-17, 2008 and presents three papers. Assoc Prof. Ueda attended the ISE annual meeting, Seville, Spain, Sep.7-12, 2008, and presented a paper entitled by “Electrodeposition of Sb-Te alloy in $AlCl_3$-NaCl-KCl molten salt”.

Presentations

Electrodeposition of Bi-Sb-Te thermoelectric material by molten salt electrolysis and it’s thermoelectric property, S. Tsuchiya, M. Ueda and T. Ohtsuka , Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 23-24, 2008

Corrosion resistance of Al-Zn-Cr alloy electroplating on mild steel, A. Munekata, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 23-24, 2008

Effects of amount of salt and temperature for corrosion products at cut-edge of galvanized steel, K. Nishimoto and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran Institute of Technology, Muroran, January 23-24, 2008

Time change of corrosion resistance of conductive polypyrrole film doped molybdate ion on 55%Al-Zn coated steel, H. Ryu, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Muroran

Institute of Technology, Muroran, January 23-24, 2008

Moisture absorption of rust layer of weathering steel after long time period exposure, H. Iwasaki and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Hokkaido University, Sapporo, January 29-30, 2008

Oxide formation on Co-Pd alloy electrode as a PEFC cathode, Y. Tamura, K. Taneda and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, January 29-30, 2008

In-situ Raman spectroscopy of iron passive film in boric acid solution, K. Taneda and T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn, and Jpn Soc. Corros. Eng., Hokkaido University, Sapporo, January 29-30, 2008

Polypyrrole coating for corrosion prevention of steels, T. Ohtsuka and D. Kowalski, International mini-Symposium on Control and Analysis of Reactions on Electrode/Solution Interface in Atomic/Molecular Resolution, Sapporo, Hokkaido University, March 10, 2008

Pyrrole coating with self-healing properties for corrosion protection of carbon steel, D. Kowalski, M. Ueda and T. Ohtsuka, International mini-Symposium on Control and Analysis of Reactions on Electrode/Solution Interface in Atomic/Molecular Resolution, Sapporo, Hokkaido University, March 10, 2008

In-situ detection of thin oxide films on electrode surface by normal Raman spectroscopy, K. Taneda, Y. Tamura and T. Ohtsuka, International mini-Symposium on Control and Analysis of Reactions on Electrode/Solution Interface in Atomic/Molecular Resolution, Sapporo, Hokkaido University, March 10, 2008

Raman spectroscopy of corrosion products at cut-edge part in zinc coated steel-influence of amount of NaCl on the steel and relative humidity-, K. Nishimoto, Student symposium on Hokkaido branch of Spectroscopical Society of Japan, Sapporo, Hokkaido University, March 13, 2008.

Corrosion resistance of Al-Zn-Cr alloy electroplated in molten salt on mild steel, M. Ueda, A. Munekata and T. Ohtsuka, The Surface Finishing Society of Japan, Chiba, College of Industrial Technology, Nihon University, March 12-14, 2008

Theory and experiment results of passive film on metal, T. Ohtsuka, Society of Materials Engineering for Resources of Japan, Akita, Akita University, March 15, 2008

Improvement of corrosion resistance of conductive polypyrrole film doped molybdate ion on 55%Al-Zn coated steel, T. Ohtsuka and H. Ryu, Meeting of ISIJ, March 25-27, 2008

Self-healing of the conductive polypyrrole coating for the corrosion protection of steels, T. Ohtsuka and D. Kowalski, Electrochemical Society of Jpn, Faculty of Engineering, Yamanashi University, Kofu, March 29-31, 2008

In-situ Raman spectroscopy of passive film on iron, T. Ohtsuka and K. Taneda, Electrochemical Society of Jpn, Faculty of Engineering, Yamanashi University, Kofu, March 29-31, 2008

The relationship between the surface oxide of Pd-Co alloy electrodes and PEFC cathode oxygen reduction reaction, Y. Tamura, K. Taneda, M. Ueda and T. Ohtsuka, Electrochemical Society of Jpn, Faculty of Engineering, Yamanashi University, Kofu, March 29-31, 2008

In-situ Raman spectroscopy for oxide thin films on Pt-Co alloy cathode catalysts for PEFC, K. Taneda, Y Tamura, M. Ueda and T. Ohtsuka,Electrochemical Society of Jpn, Faculty of Engineering, Yamanashi University, Kofu, March 29-31, 2008

Electrodeposition of Bi-Sb-Te thermoelectric material by pulse electrolysis in chloride molten salt, M. Ueda, S. Tsuchiya and T. Ohtsuka, Electrochemical

Society of Jpn, Faculty of Engineering, Yamanashi University, Kofu, March 29-31, 2008

Raman spectroscopy for oxide thin films on Pt-Co alloy cathode catalysts for simulated PEFC cathode situation, K. Taneda, Y. Tamura, M. Ueda and T. Ohtsuka, Zairyo-to-Kankyo 2008 Annual Meeting, Omiya Sonic-city, Omiya, May 13-15, 2008

Influence of surface oxide on Pd-Pd alloy electrodes for PEFC cathode oxygen reduction reaction, Y Tamura, K. Taneda, M. Ueda and T, Ohtsuka, Zairyo-to-Kankyo 2008 Annual Meeting, Omiya Sonic-city, Omiya, May 13-15, 2008

Moisture adsorption, electrical conductivity, and near-infrared light spectroscopy of rust layer on weathering steel after long time period exposure, H. Iwasaki and T. Ohtsuka, Zairyo-to-Kankyo 2008 Annual Meeting, Omiya Sonic-city, Omiya, May 13-15, 2008

Electrochemical behavior and alloy deposition of Bi, Sb, and Te in chloride molten salt, M. Ueda, H. Ebe, S. Tsuchiya and T. Ohtsuka, 166th molten salts committee meeting, Morioka, May 29-30, 2008

Investigation of propylene carbonate as a electrolytic melt for Na electrorefining process, H. Hayashi, M. Ueda and T. Ohtsuka, A meeting of Hokkaido branch of The Chemical Society of Japan, Kitami Institute of Technology, Kitami, July 19, 2008

Corrosion evaluation of fishhook in environment-conscious longline, S. Tanaka, T. Ohtsuka and K. Miyakoshi, Summer Meeting of Hokkaido Branch of Jpn Inst. Metals and ISIJ, Hokkaido University, Sapporo, July 24-25, 2008
Effect of oxide film on oxygen reduction current for the platinum-cobalt alloy electrode in PEFC, Y. Tamura, K. Taneda, M. Ueda and T. Ohtsuka, International Symposium on Anodizing Science and Technology (AST 2008), Rusutsu,

July23-25, 2008

Photoluminescence from passive oxide films on nickel and chromium by photo-excitation of UV light, Y. Mito, M. Ueda and T. Ohtsuka, International Symposium on Anodizing Science and Technology (AST 2008), Rusutsu, July 23-25, 2008.

Electrodeposition of Sb-Te alloy in $AlCl_3$-NaCl-KCl molten salt, M. Ueda, Y. Mito and T. Ohtuska, ISE annual meeting, Seville, Spain, Sep.7-12

Development of electrorefining process of Na for recycle of Na-S secondary battery, M. Ueda, Innovation Japan 2008, Tokyo International Forum, Tokyo, September 16-19, 2008

Photoluminescence from passive film on Cr by UV light excitation, Y. Mito, M. Ueda and T. Ohtsuka, Fall Meeting of ECSJ 2008, Kumamoto University, Kumamoto, September 23-25, 2008

Electrochemical measurement of sodium in propylene carbonate containing $NaPF_6$, H. Hayashi, M. Ueda and T. Ohtsuka, Fall Meeting of ECSJ 2008, Kumamoto University, Kumamoto, September 23-25, 2008
In-situ Raman spectroscopy for the passive oxide film on iron in neutral borate solution, T. Ohtsuka and K. Taneda, Pacific Rim Meeting on Electrochemistry and Solid-state Science (PRIME), Honolulu-Hawaii, Oct., 12-17, 2008.

Self-healing ability of conductive polypyrrole coating with artificial defect, D. Kowalski, M, Ueda and T. Ohtsuka, Pacific Rim Meeting on Electrochemistry and Solid-state Science (PRIME), Honolulu-Hawaii, Oct., 12-17, 2008

Surface oxide film and its influence on the oxygen reduction on Pd-Co and Pt-Co PEFC cathodes, Y. Tamura, K. Taneda, M. Ueda and T. Ohtsuka, Pacific Rim Meeting on Electrochemistry and Solid-state Science (PRIME), Honolulu-Hawaii, Oct., 12-17, 2008

Ion-Exchange Treatment of Glass Surface in Molten Salt, Y. Tabei, M. Ueda, T. Ohtsuka and T. Yamashita, 8th International Symposium on Molten Salts, Kobe, October 19-23, 2008

Electrodeposition of Bi-Sb-Te alloy in molten salt, M. Ueda, S. Tsuchiya and T. Ohtsuka, 8th International Symposium on Molten Salts, Kobe, October 19-23, 2008

Facilities and Capabilities

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light.
Potential Modulation Reflectance: Wavelength region from 350 to 800 nm.
Raman Scattering Spectrometer: JASCO R-800T, triple type of spectrometer equipped with an Argon gas laser of 2W power.
Raman Scattering Spectrometer: Bonko Keiki, single type of spectrometer equipped by high sensitive CCD.
FT-IR Spectrometer: JASCO FT/IR 550 equipped with MCT detector for in-situ measurement of corrosion layers on metals.
QCM system for in-situ gravimetry of surface layer on metals.
Electrochemical AC Impedance: NF Circuit Design 5020 FRA and 5095 FRA equipped with a specially designed potentiostat.
Spectrophotometer: JASCO V-520 in a wavelength region from 200 to 900 nm.
ICP atomic emission spectrometer: Thermo i-CAP 6000.
Electrochemistry apparatuses.
Optical Microscopy
Electrochemical Corrosion Rate Monitor System.

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The research activities of the laboratory are directed to the development of advanced oxide films and nanomaterials utilizing anodic oxidation process and spin coating. We are also interested in surface analytical techniques with nanoscale resolution for a better understanding of the interfacial phenomena of metal and semiconductor electrodes in relation to electrochemical devices for energy storage, corrosion, passivation and surface finishing.

Current topics on research are as follows:

(1) Formation of barrier-type anodic oxide films on niobium and titanium alloys for capacitor application

Novel anodic oxide films with excellent dielectric properties have been tailored on non-equilibrium, single phase niobium and titanium alloys for replacing the currently used tantalum solid capacitors. Structural modification of the anodic films by incorporation of alloying elements is a key issue to improve the dielectric properties. Advanced process using physical vapor deposition has now been investigated to develop a porous electrode for electrolytic capacitor application. Utilization of substrate with cellular structure is effective to tailor alloy nano-columns with controlled gaps between columns. Our findings revealed high potential of porous non-equilibrium Nb-Si and Ti-Si alloys prepared by PVD technique for capacitor application.

(2) Tailoring of self-organized porous anodic oxides on various valve metals

Recently, we have found that phosphate-glycerol solution at elevated temperature is a new electrolyte to form self-organized porous anodic films on various valve metals. We have already successfully developed self-organized porous anodic films on Ti-Si alloys, niobium and aluminum in the hot phosphate-glycerol electrolyte. The importance of water content in the electrolyte has been found for the growth of anodic film on niobium. The reduction of water content increases the growth rate and promotes the incorporation of phosphate anions in the anodic films. SIMS depth profile revealed that oxygen source of the anodic film was residual water in the electrolyte. Thus, the control of water content is crucial for the formation of porous anodic films.

(3) Spark anodizing for development of thick oxide films with excellent wear and corrosion resistance

Spark anodizing of titanium alloys has been performed to form hard and adhesive oxide ceramic coating to improve the wear resistance of various titanium alloys. Similar coatings with high hardness have been developed on Ti, Ti-6Al-4V and Ti-15V-3Al-3Cr-3Sn. However, the adhesion of the coating developed on

Ti-15V-3Al-3Cr-3Sn was relatively poor. The poor adhesion was associated with void formation in the inner layer close to the alloy/film interface. Spark anodizing has been also applied to magnesium alloys to improve the corrosion resistance.

(4) Surface characterization using glow discharge optical emission spectroscopy

Radio frequency glow discharge optical emission spectroscopy (rf-GDOES) with excellent depth resolution of sub-nanometer scale has been used to analyze thin anodic films as well as passive films. The excellent depth resolution even for non-conducting layers and extremely high sputtering rate allow obtaining depth profiles precisely and quantitatively. Depth profiles of molybdenum species in the passive films on molybdenum-containing stainless steels have been analyzed to elucidate the role of molybdenum in enhancing the passivity.

(5) Proton-conducting oxide nanofilms prepared by spin coating

Gas-tight silicate and phosphate nanofilms have been prepared by spin coating and proton conductivity in the nanofilms have been examined after depositing gold or platinum button electrode. The nanofilms showed efficient proton conductivity, and interestingly, the conductivity was enhanced markedly by reducing the film thickness to less than ~100 nm. Such scaling behavior has been analyzed in terms of a percolation model.

Other Activities

In July, Prof. H. Habazaki organized International Symposium on Anodizing Science and Technology (AST2008) as a secretary general. In this symposium, Dr. D. Kowalski, Mr. M.T. Tanvir, Mr. Y. Miura, Mr. T. Fujii, Mr. M. Uemura had poster presentations. Mr. T. Fujii received a Best Poster Award in this symposium. In September, Prof. H. Habazaki participated 59th Annual Meeting of International Society of Electrochemistry, Seville, Spain and presented a paper entitled "Formation and Wettability of Microcone-Type Porous Anodic Films on Niobium". In October, Prof. H. Habazaki and Dr. Y. Aoki participated PRiME 2008, Honolulu, USA and presented a paper entitled "Growth of Porous Anodic Films on Niobium in Hot Phosphate-Glycerol Electrolyte" and "Enhanced proton conductivity of amorphous silicate nanofilms". In November, Prof. H. Habazaki was invited in the

3rd Asian Symposium on Electrochemical Power Sources and presented a paper entitled “Template-assisted Synthesis of Solid Hollow Carbon Nanofibers and Their Electrode Properties for Electrochemical Capacitors”.

Presentation

T. Fujii, Y. Aoki, K. Fushimi, T. Makino, S. Ono, H. Habazaki; Formation of porous aluminum films by PVD for electrolytic capacitor application, International Symposium on Anodizing Science and Technology (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008).

M. Nakajima, Y. Miura, K. Fushimi, H. Habazaki; Spark anodizing behaviour of Titanium and its alloys in alkaline aluminate electrolyte, International Symposium on Anodizing Science and Technology, (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008).

M. Tauseef Tanvir, Y. Aoki and H. Habazaki; Formation of porous niobium films by oblique angle deposition: influences of deposition angle and substrate morphology, International Symposium on Anodizing Science and Technology, (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008).

D. Kowalski, Y. Aoki, and H. Habazaki; Electronic behavior of amorphous anodic Nb_2O_5 nanofilms in ambient gas atmospheres, International Symposium on Anodizing Science and Technology (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008).

S. Yamamoto, K. Fushimi, H. Habazaki and H. Konno; Diffusion limiting-current equation in the flowing-type droplet cell, International Symposium on Anodizing Science and Technology (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008).
M. Uemura, T. Yamamoto, Y. Aoki, K. Fushimi, H. Habazaki; GDOES depth profiling analysis of thin passive films on molybdenum-containing stainless steel”,

International Symposium on Anodizing Science and Technology (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008).

T. Yamamoto, K. Fushimi, H. Habazaki, H. Konno; Repassivation behavior of passive film on pure iron in borate buffer solution investigated by micro-indentation, International Symposium on Anodizing Science and Technology, (AST2008), 2008.7.23-25, Rusutsu, Hokkaido, Japan (2008)

K. Fushimi, H. Habazaki, S. Yamamoto; Micro-electrochemistry with Flowing Electrolyte-type Scanning-droplet-cell, 59th Annual Meeting of International Society of Electrochemistry, 2008.9.9, Seville, Spain (2008).

Y. Oikawa, T. Minami, H. Mayama, K. Tsujii, K. Fushimi, Y. Aoki, H. Habazaki; Formation and Wettability of Microcone-Type Porous Anodic Films on Niobium, 59th Annual Meeting of International Society of Electrochemistry, 2008.9.10, Seville, Spain (2008).

M. Seo: Changes in Surface Stress of Au (111) Electrode during Underpotential Deposition of Bi, Pb or Cu, Seminar, Institute of Nanotechnology, 2008.9. 10, Karlsruhe, Germany (2008).

Y. Oikawa, K. Fushimi, Y. Aoki, H. Habazaki; Growth of Porous Anodic Films on Niobium in Hot Phosphate-Glycerol Electrolyte, PRiME 2008-214th ECS Meeting, 2008.10.12-17, Honolulu, USA (2008).

Y. Aoki, H. Habazaki and T. Kunitake; Enhanced proton conductivity of amorphous silicate nanofilms, PRiME 2008-214th ECS Meeting, 2008.10.12-17, Honolulu, USA (2008).

D. Kowalski, Y. Aoki, H. Habazaki; Characterization of amorphous anodic Nb_2O_5 nanofilm for gas sensing, PRiME 2008-214th ECS Meeting, 2008.10.12-17, Honolulu, USA (2008).

T. Fujii, Y. Aoki, K. Fushimi, T. Makino, S. Ono, H. Habazaki: "Oblique Angle Deposition of Porous Al-Nb Alloys for Electrolytic Capacitor Application", PRiME 2008-214th ECS Meeting, 2008.10.12-17, Honolulu, USA (2008).

M. Seo, N. Kikuchi, K. Fushimi, H. Habazaki, T. Nakayama: Anodic Behavior of Nickel in Acidic Perchlorate Solution Containing Pb^{2+}, PRiME 2008-214th ECS Meeting, 2008.10.12-17, Honolulu, USA (2008).

H. Habazaki, M. Kiriu, K. Fushimi and H. Konno: “Template-assisted synthesis of solid and hollow carbon nanofibers and their electrode properties for electrochemical capacitors”, 3rd Asian Symposium on Electrochemical Power Sources, 2008.11. 10-14, Seoul, Korea (2008).

D. Kowalski, Y. Aoki, H. Habazaki: “Characterization of Anodic ZrO_2-WO_3 Films in Ambient Gas Atmospheres”, The 2nd GCOE International Symposium Hokkaido University Global COE Program, 2008.12.18-19, Sapporo, Japan (2008).

Facilities and Capabilities

DC and RF magnetron sputtering: Shimadzu SP-2C, suitable for preparation of various metallic thin films as well as oxide and nitride films.
Laser Raman Spectrometer: Jobin Yvon T64000, triple type spectrometers with an argon gas laser of 2W.
FT-IR spectrometer: Jasco FT-IR350, equipped with DR and RAS attachments.
Ultramicrotomy: RMC MT-7, suitable for the preparation of electron transparent TEM sections.
AFM: SII SPA-400 system operating in contact and tapping modes.
Impedance analyzer: Solartron 1260, measureable in the frequency range of 10 μHz to 32 MHz.

LABORATORY OF HIGH TEMPERATURE MATERIALS

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Research work at “Laboratory of high temperature materials” directs toward 1) high-temperature corrosion of Cr-Si-Ni and CoNiCrAlY alloys, 2) high-temperature oxidation of metal disilicides in H_2O-containing atmospheres, 3) microstructures of oxide scales formed on NiAl-X alloys, 4) development of advanced high-temperature materials of Nb-Si-B system, 5) structures of oxide scales formed on carbon steels, stainless steels and aluminum alloys in H_2O -containing atmospheres, and 6) corrosion behavior of iron-based alloys in molten lead-free solders.

Current topics on research are in the following:

(1) High-temperature corrosion behavior of Cr-Si-Ni alloys

High-temperature corrosion tests of Cr-Si-Ni and CoNiCrAlY + X (X=Si, Cr) alloys are being carried out. The Cr-Si-Ni and CoNiCrAlY alloys have excellent corrosion resistance to molten Na_2SO_4 and NaCl salts, comparing with STBA21. This result showed that SiO_2 and/or Al_2O_3 scale is very effective for preventing sulfidation and chlorination of the alloys.

(2) Oxidation behavior of metal disilicides in H_2O-containing atmospheres

In order to clarify the effects of B addition on the formation of protective oxide scales on B added disilicides in H_2O-containing atmosphere, evaporation behavior of B-SiO_2 was examined. The results demonstrated that the addition of B to SiO_2 led to the formation of borosilicate and the suppression of evaporation of SiO_2. In addition, the addition of B led to improvement of plasticity of SiO_2 (prevention of cracking).

(3) Microstructures of oxide scales formed on NiAl-X alloys

In order to clarify the microstructures of oxide scales formed on NiAl-X alloys, the oxidation tests in air have been performed. Microstructures of the oxide scales formed on NiAl-X alloys are being observed by FIB-TEM and analyzed by EDS. The addition of Si has no effect on the growth rate of oxide scale. The sizes of interfacial voids observed in the sample with Si addition were larger than those of the sample without Si. However, the addition of Mo suppresses the formation of such voids. These results imply that the effect of Si addition is to degrade the adherence of oxide scale, and that of Mo addition is to improve the adherence.

(4) Development of advanced high-temperature materials of Nb-Si-B system

Nb-X/$NbSi_2$ and Nb-X/ $NbSi_2$-B diffusion couples were heated up to 1573-1773K, and kept for up to 4 hours. Interfacial reaction layers formed during annealing were observed and analyzed by using SEM and EPMA. The addition of Ti to Nb has a slight effect on the suppression of growth of interfacial reaction layer because of the formation of B enriched layer at the interface between Nb-X and $NbSi_2$ or $NbSi_2$-B. On the other hand, the addition of Cr and Si promotes the growth of interfacial reaction layer. Moreover, the addition of Al to Nb has no effect on the growth rate of the interfacial reaction layer.

(5) High-temperature oxidation of carbon steels, stainless steels and aluminum alloys in H_2O-containing atmospheres

In order to clarify the microstructures of oxide scales formed on Al-Mg alloys with various Mg concentrations, oxidation tests are in progress in H_2O-containing atmospheres. The thickness of oxide scale (mainly MgO scale) increased as the Mg concentration in the alloys and water vapor concentration in the atmospheres increase. Moreover, the effect of water vapor on the formation of oxide scale is being studied by FIB-TEM. Similarly, oxidation behavior and scale structures of carbon steels and stainless steels in H_2O-containing atmospheres are also being investigated. For carbon steels we have investigated the craching and/or spalling behavior of oxide scales during cooling using the acoustic emission technique. The result showed that the presence of water vapor and the increase in Si content in the carbon steel tend to promote the scale failure.

(6) Corrosion behavior of iron-based alloys in molten lead-free solders

The research on corrosion of Fe-X (X=Cr and Ni) alloys in molten lead-free solders such as Sn-Ag-Cu is in progress. The thickness of consumed substrate decreases with increasing the concentration of Cr and Ni. The inner layer formed between outer reaction layer and Fe-based substrate suppresses the inward Sn diffusion from solder or outward Fe diffusion from substrate. Moreover, we investigated the influence of alloying elements on the formation of the sub-grains in primary Sn grains of the solidified solder. The addition of Al and Bi has an excellent effect on the formation of finer sub-grains in primary Sn grains.

Other Activities

In March, Prof. Kurokawa attended “The lst Inter’l Workshop on Plasma Application and Hybrid Functionally Materials” held in Dalian, China, and presented papers entitled “Microanalysis of Oxide Scale Formed on Sintered Cr-Si-Ni”.

Presentations

Formation and degradation of Cr_2O_3 scale in atmospheres containing mixed oxidants at high temperatures; K. Kurokawa: NIMS seminar, Tokyo, Jan., 2008.

Effect of water vapor on morphology of alumina scale formed on NiAl alloys; H. Tomoto, A. Yamauchi, S. Watanabe, K. Kurokawa and T. Narita: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Sapporo, Jan., 2008.

Microstructure of oxide scale formed on Cr-Ni-Si compacts in air and H_2O-containg atmospheres; Y. Suzuki, A. Yamauchi and K. Kurokawa: ibid

Experimental study on Re-Ni binary phase diagram; S, Saito, K. Kurokawa, T. Takashima, S. Hayashi and T. Narita: ibid

Effect of additional elements on formation of sub-grain in Sn-besed solders; H. Takaki, A. Yamauchi, K. Kurokawa and J. Tanaka: The Joint Meeting of The Hokkaido Sections of ECS Jpn., Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Jan., 2008.

Effect of additional elements on corrosion behavior of Fe-based alloys in molten lead-free solders; A. Yamauchi, K. Kurokawa and J. Tanaka: ibid

Interfacial microstructure of Fe-based alloys corroded in molten lead-free solders; A. Yamauchi, J. Irizawa, S. Kawakubo, K. Kurokawa and J. Tanaka: Mate2008, Yokohama, Feb., 2008.

Microanalysis of Oxide Scale Formed on Sintered Cr-Si-Ni; Y. Suzuki, A. Yamauchi, and K. Kurokawa: The lst Inter'l Workshop on Plasma Application and

Hybrid Functionally Materials, Dalian, China, March, 2008.

Evaluation of phase stability of diffusion barrier coating by experimental phase diagram – phase stability of σ phase in Re-Cr-Ni-Al system at 1423 K -; S. Saito, K. Kurokawa, T. Takashima, S. Hayashi and T. Narita: The 15th Annual Meeting of Jpn. Inst. Metals, Tokyo, Mar., 2008.

Evaporation behavior of SiO_2-B_2O_3 compacts in H_2O-containing atmospheres; K. Tanaka, A. Yamauchi and K. Kurokawa: ibid

Oxidation behavior of $Si_{6-z}AI_zON_{8-z}$(z=1,3,4) in H_2O-containing atmospheres; A. Yamauchi, K. Aoyagi, R. Sivakumar, T, Akiyama and K. Kurokawa: ibid

Effect of Si addition on the microstructure of oxide scale formed on β-NiAl; T. Ito, A. Yamauchi and K. Kurokawa: The Spring Joint Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Sapporo, July, 2008.

Morphology change of oxide scales formed on Al-Mg alloys in H_2O-containing atmospheres; T. Kurosaki, A. Yamauchi and K. Kurokawa: ibid

Oxidation behavior of ferritic stainless steels with Mo; T. Shoji, A. Yamauchi and K. Kurokawa: ibid

Effects of additional eletements on formation of sub-grain in Sn alloys; H. Takaki, A. Yamauchi, J. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: The 18th Symposium of Micro Electronics, Kyoto, Sep., 2008.

Effects of alloying elements on corrosion behavior of Fe-based alloys; A. Yamauchi, S. Kawakubo, J. Irisawa, K. Kurokawa and J. Tanaka: ibid

Oxidation behavior of ferritic stainless steels with Mo in H_2O-containing atmospheres; T. Shoji, A. Yamauchi, K. Kurokawa, K. Fukuda, S. Ishikawa and T.

Ujiro: The 155th ISIJ Meeting, Kumamoto, Sep., 2008.

Fabrication of Nb/$NbSi_2$ having the ultra-high temperature oxidation resistance－Oxidation resistance of B-$NbSi_2$ and its adaptability for Nb alloys－; M. Ukegawa, A. Yamauchi and K. Kurokawa: The 142th Annual Meeting of Jpn. Inst. Metals, Kumamoto, Sep., 2008.

Fabrication of B-WSi_2 having the excellent oxidation resistance; K. Tanaka, A. Yamauchi and K. Kurokawa: ibid

Effects of Si and Mo addition on morphology of oxide scale formed on β-NiAl; T. Ito, A. Yamauchi, K. Kurokawa and T. Narita: ibid

Morphology of oxide scales formed on Al-Mg alloys; T, Kurosaki, A. Yamauchi, K. Kurokawa and A. Fukumoto: ibid

Optimum composition of Al-reservoir as a diffusion barrier coating; S. Saito, K. Kurokawa, T. Takashima, S. Hayashi and T. Narita: ibid

Facilities and Capabilities

Spark Plasma Sintering Equipment
Ultra-High Vacuum Furnace with Mass Spectrometer
Oxidation Test Equipment with Thermobalance and Ultra-High Temperature Furnace
Optical Microscope with High-Temperature Furnace
Micro-Thermobalance
SEM (Carry Scope)
Micro Vickers Hardness Tester
Acoustic Emission System

BIOMEDICAL, DENTAL MATERIALS AND ENGINEERING LABORATORY

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The research activities cover (1)the development, evaluation and application of dental and biomedical materials, (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 microanalyses. Many researches are related to dental, biological and engineering fields and performed in collaboration with clinical departments including Removable Prosthetic Dentistry(Prof. Atsuro Yokoyama), Orthodontics

(Prof.Junnichiro Iida), Operative Dentistry (Prof.Hidehiko Sano), Oral and Maxillofacial Surgery(Prof.Yasunori Totsuka), Crown and Bridge Prosthodontics (Prof.Noboru Ohata) and Protective Dentistry(Prof.Manabu Morita).
Current topics on research are as follows;

(1) Biocompatibility and biomedical application of carbon nanotubes (CNT) and other fine particles

Biocompatibility and cytotoxicity of carbon nanotubes (CNT), carbon nanofibers (CNF), fullerene and other nano materials were investigated. Various type of CNT including single and muti-wall CNTs (SWCNT, MWCNT) and CNF were used with the aim of the biomedical application and the pretreatment method of purification, solubilization, dispersion, surface modification were developed. Biochemical cell functional test of cell survival rate, LDH activity, emission of oxygen radicals and cytokines IL-1β, IL-8, TNF-α, M-CSF and implantation test in soft tissue was done and bioreaction was evaluated. With the decrease of particle size the cytotoxicity originated from the physical size effect was pronounced especially below 10μm. Many interesting properties advantageous to buomedical application such as affinity for adhesion of cells, proteins,saccharides; precipitation of apatite in artificial salivary fluid and strong binding of pseudopodium grown into the agglomeration of CNTs as scaffold, Applications of the monotubes as delivery system of DNA, protein, saccharic tips and the sintered bulk as implant materials are also developed.

(2) 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.

(3) Modifications of carbon nanotubes for biological applications

For biomedical applications of carbon nanotubes (CNTs), new modification methods to give bioactivity or biocompatibility are needed for achievement of various required designs. Modification and immobilization of various functional molecules on CNTs by covalent and non-covalent methods were investigated. Multi-walled carbon nanotubes (MWNTs) coated with a carbohydrate-carrying polymer can be easily prepared by a non-covalent and via hydrophobic interactions. The carbohydrate coated MWNT was found to acquire a selective binding affinity to the corresponding lectin without a nonspecific interaction. On the other hand, a bare MWNT interacted nonspecifically with lectins. These results showed that a MWNT coated with a carbohydrate-carrying polymer has the biological recognition signals. Secondly, we developed a biomimetic coating method to produce the architecture of crystalline apatite at nano-scale levels on the surface of MWNTs. After immersion of MWNTs in revised simulated body fluid (r-SBF), the crystallites at nano level were grown radially originating from a common center in the middle of a single MWNT and perpendicularly to the longitudinal direction of MWNT. MWNTs with the defined surface morphology of nano apatite crystallites could be useful as biomaterials for scaffolds and for the biomedical applications.

(4) Development of FRP esthetic orthodontic wire

To realize the esthetic, transparent orthodontic wire the FRP wires of the diameter 0.5mm with the multiple fiber structure has been fabricated by either drawing of fiber-polymer complex at 250C or photopolymerization method. Biocompatible $CaO-P_2O_5-SiO_2-Al_2O_3$ (CPSA) glass fibers of 8-20μm 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.

(5) Cytotoxicity due to ions and fine particles of Ti and other metals in vivo and in vitro:

The removal of Ti plates for fixing jaw bone in 6 months after operation often reveals the slightly dark colored tissue in the circumferential soft tissue. The observation and analysis by optical microscopy, electron microscopy and XSAM revealed that the colored tissue contains the abraded fine particles of Ti, probably produced during plate fixation in operation.

The animal experiments to implant various sizes of Ti particles of 1-100μm and macroscopic cylindrical Ti implant in μm order for 3 days to 8 months showed that the macroscopic size of Ti was encircled with fibrous connective tissue layer from early stage and there was no inflammation. As the size of particle becomes smaller, many phagocytic cells appear with fibrous connective tissue layer inside the particle inserted region and tissue showed inflammation. It takes more time to encircle the particle-contained tissue region and heal inflammation. For 1-3μm the inserted region is never encircled with fibrous connective tissue layer and inflammation continues.

The in vitro cell functional tests on cell survial rate, LDH(Lactate Hydrogenase CII) protein released at the breakdown of cell membrane and superoxided anion (O^{2-}) sing human neutrophils showed that Ni solution has he cell disruption effect. The deformed and disrupted morphology of neutrophils was confirmed by SEM observation. Whilst Ti and V solution showed the increase of superoxide anion and negligible change in the others, which suggests the cell stimulation effect. SEM observation confirmed that neutrophis are inflated with more complicated polyacicular morphology. One of the marking cytokines released at phagocytization, TNF-α, was not detected in any solution of Ni, V, Ti, the simulated body fluid(Hank's solution) mixed with 10mm paricles of Ti and with submicron size Ni particles. TNF-α was found only in the 1-3μm Ti particle mixed Hank's solution, which suggests that particles were phagocytized. SEM observation and EDS elemental analysis confirmed the phagocytosis of Ti particles by neutrophils.

The difference of cell reaction to 1-3µm and 10µm Ti particles suggests that the particles(1-3µm) smaller than cell size(about 5µm in neutrophils) induces cytotoxicity as a result of phagocytosis, while for particles larger than cell size(10µm) phagocytosis is not possible, resulting in the less clear cytotoxicity effect.

The study shows the cytotoxicity originating from physical size effect of particles other than biochemical toxicity effect, which is significant for the cases where the fine particles are produced during abrasion by long term usage of moving parts in the artificial bone joint.

(6) 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.

(7) Fabrication of composite resin prostheses by laser lithography:

Laser lithography, one of the CAD/CAM systems to fabricate the polymer models by piling up the thin slices, which are photo-polymerized by scanning laser beam originally on the shallow depth of liquid epoxy monomer, was applied for the fabrication of dental prosthoses of photo-curing composite resin composed of silica fillers in the matrix of high strength UDMA resin. The full dental crown could be fabricated using the shape data pre-designed by computer with high accuracy due to the smaller polymmerization shrinkage than by conventional methods. Then the functionally graded dental core and post with gradually changing filler content from 70 to 0% from the head of core abutment toward the apex of post was successfully fabricated. The stress concentration at the pulp root inserted with the conventional dental post has often caused the fracture in the surrounding dentin by impact force on the tooth crown. The stress relaxation effect by application of the functionally graded dental post was confirmed by simulation using the photoelastic method and finite element method (FEM).

(8) Radiation effects on polymer resin:

Radiation effects by C^+ion, γ-ray from Co^{60} and electrons on one of the main matrix polymer UDMA (urethane dimethacrylate) for dental composite resin were investigated with various mechanical tests and spectroscopies. C^+ion radiation induced the large change in the structure sensitive properties of mechanical properties, Vickers hardness, flexural strength, abrasion resistance and little change in the non-structure sensitive properties of spectroscopies, FT-IR, Raman scattering, Fluorescence, NMR and thermal expansion coefficient. The results suggest that the mechanism of radiation effect is mostly due to the physical structure change such as lattice defects of vacancies, interstitials, depleted zone rather than the chemical effect of cross-linking by further progress of polymmerization of residual monomers.

(9) 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.

(10) 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 was improved.

(11) 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.

(12) Bonding property and cytotoxicity of dental zirconia ceramics (YPSZ)

Yttria partially stabilized zirconia (YPSZ) ceramic is suitable for dental and medical use because of its high fracture toughness and chemical durability. The bonding properties of dental zirconia with various luting cements and surface treatments are investigating. The cytotoxicity dental zirconia ceramics compared to other dental ceramics was also evaluated.

(13) Abrasion-resistant implant made of refractory metal nitrides and carbides

Surface-nitrided titanium (Ti (-N)) showed high corrosion resistance and nearly equivalent biocompatibility with Ti in soft and hard tissue in animal implantation test. Surface durability was evaluated by three static and dynamic mechanical tests; Vickers hardness test, Martens scratch test and for more practical viewpoint newly developed abrasion test using ultrasonic dental scaler which is used to remove calculus on teeth in dental clinics. Vickers hardness of Ti(-N) was 1300, ten times larger than Ti. Martens scratch test showed that the bonding of nitrided layer with 2μm thickness is coherent to matrix Ti and enough strong. Abraded volume by ultrasonic scaler was increased with the load in Ti, while no trace was formed in Ti-(N), instead stainless tip of scaler was abraded. The test showed that abrasion would be negligibly small under the practical conditions of the load 50g in clinics. Ti-(N) with biocompatibility and surface abrasion resistance would be suitable as abrasion-resistant implant materials for the application to the artificial joint of implant and abuttment part of dental implant.

(14) Development of visible-light responsible photocatalysis and its application

The current photocatalysis of anatase TiO_2 mostly works only by ultraviolet light. To make applicable for medical use it is necessary to develop the visible-light reactive photocatalysis. Visible light sesitization was obtained by surface modification with caions of Au, Ag, Cu, Pt, and Pd. Depigmentation with visible light around 470nm which is used for photopolymerization of composite resin restoration in dental clinics could be done with the Ag activated TiO_2 in contrast to very little effect in an untreated TiO_2. Antibacterial effect was also confirmed to streptococcus mutans, one of the most popular bacteria for caries. The application to bleaching of pigmented teeth was developed.

(15) Development of discrimination method of resin-restored teeth

In the health checkup in school mass of patients must be checked in the limited time. Due to the recent development of estheticity of composite resin it is now very difficult to recognize the resin-restored teeth and discern resin part from natural teeth. Total reflection spectroscopy and fluorescence spectroscopy were measured and images were taken with reflected light and fluorescence light using the filters to select the appropriate wave length. In the long wave length region for more than 600nm the reflectivity of teeth is higher than that of composite resin. The image formed with filtered light, however, did not show the contrast enough to discern the resin part from tooth. For less than 400nm both teeth and resin showed the fluorescence emission with high and comparable intensity. For the light of 430-450nm teeth emitted higher fluorescence and the relative difference is larger. The images formed with fluorescence light for more than 500nm emitted by 430-450nm light excitation showed the easily recognized contrast to discriminate resin from tooth.

(16) Microparticles of biodegradable polymers with controlled structure for drug delivery system

Single and double emulsification solvent evaporation method is extensively used for more than two decades for the encapsulation of various substances form simple pharmaceutical products to proteins and DNA.

Particle formation mechanism is crucial for size distribution, and morphology, which in turn determine the delivery system behavior during encapsulation and release.

In order to identify and quantify the main influence parameters those determine the microparticle performance as drug delivery system, the mechanism of particle formation of biodegradable polyesters: poly (DL-lactide co glycolide) and poly (L-Lactide), was investigated in their single and double emulsion formulation.

In situ optical microscopic investigations showed that the microparticles are formed by accelerated solvent elimination due to the combined effects of high solvent volatility and polymer precipitation. The fast shrinkage that accompanies the solvent elimination has important influence on the particle morphology. Scanning electron microscopy and laser diffractometry evidenced the presence of a thin nanoparticulate layer on the microparticles surface. This layer is formed during the solvent elimination by the shrinkage-induced fragmentation of the precipitating polymer. It is reasonable to believe that the encapsulated substance will accumulate in this layer contributing to the initial burst release.

The inner aqueous phase in the double emulsion formulations has important influence on the mechanism of particle formation. In this case microparticles with different structures are generated. The proportions of microparticles with different structure are determined mainly by the stirring rate and the polymer concentration.

During solvent elimination the droplets of inner aqueous phase coalesce under the precipitating polymer pressure. Due to the incompressibility of the inner aqueous phase, the polymer wall often breaks resulting in holes through which the inner aqueous phase is partly expulsed. Furthermore, after particle hardening the holes will contribute to the encapsulated substances leakage through partitioning with the external aqueous phase, and to the initial burst release.

Other activities:

International Symposium on "Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes" (ISNT2008) was promoted by Prof. Watari as the Chairman on June 16-17, 2008 at Conference Hall in Hokkaido University. This symposium was helded in the Hokkaido University “Sustainability Week 2008” that associated with G8 Hokkaido Toyako Summit 2008. Seven invited rectures, 27 oral presentations and 44 poster presentations were held with 78 from domestic and 12 from foreign attendee. Eight young researchers from Korea, Singapore, USA, Germany, France and China were invited as the Young Researcher Invitation Program of ISNT2008 with the financial support of Sustainability Week Program of Hokkaido University.

The three-year research project in nanomedicine under the subject of "Development of Visualization Method of Internal Motion of Nanoparticles (H18-Chem-General-006)" is continueing the three year as Research on Advanced Medical Technology under Health and Laybour Sciences Research Grants from the Ministry of Health, Laybour and Welfare of Japan. The project team is constitute of Leader: Prof.Fumio WATARI, Assigned Researchers: Prof.Yasunori TOTSUKA, Prof. Yoshimasa KITAGAWA, Prof. Manabu MORITA, Prof. Atsuro YOKOYAMA (Graduate School of Dental Medicine, Hokkaido University), Prof. Kiyotaka ASAKURA, Prof. Somei OHNUKI, Prof. Bunshi FUGETSU, Assoc.Prof. Haruichi TOYAMA (Hokkaido University), Prof.Kazuyuki TOHJI(Tohoku University), Prof. Kenzo ASAOKA (Tokushima University), Prof. Kunio ISHIKAWA (Kyushu University), Masayuki OKAZAKI(Hiroshima University) and other Collaborating Researchers.

The international collaborations are continued with Institute of Dental Materials Science, Umea University, SWEDEN (Emerita Prof. Maud BERGMAN) on application of Ti, ZrO_2, amalgum for dentistry, and research on side effects, with Department of Dental Materials, Chonbuk National University, KOREA (Prof.Tae-Sung BAE) on evaluation of mechanical properties of laser-welded Ti, dental porcelain, with Institute for Materials Science, Dresden Institute of Technology, GERMANY (Prof.W.POMPE) on the biocompatibility evaluation and application of collagen-hydroxyapatite composites and with Biomaterials Laboratory, Department of Materials Science and Engineering, Tsinghua University, CHINA (Prof.FZ CUI) on the development and biomedical application of nanobiomaterials, University Polytechnica Bucharest, Bucharest, Romania (Dr. ROSCA Iosif Daniel) on the development of polymer biomaterials.

The collaboration with Laboratory for Advanced Materials, Institute for Materials Research, Tohoku University (Assoc.Prof.Mamoru OMORI) is undergoing on the fabrication of new biomaterials including bulk carbon nanotubes and functionally graded materials by applying a spark plasma system(SPS) as a method to enhance sintering. The development of FRP esthetic orthodontic wire has continuously been done with Department of Industrial Chemistry, Chiba Institute of Technology (Associate Prof.Masahiro KOBAYASHI).

Presentations

Reaction of cell and tissue to material nanosizing; F.Watari, S.Abe, T.Akasaka, M.Uo, M.Matsuoka, N.Takashi, Y.Totsuka:, 17th Iketani Conference The DOYAMA Symposium on Advanced Materials, Tokyo, Sept. 5-8, 2008

Size dependence of interaction of materials with cells and tissue, Fumio Watari, Shiagaki Abe, Eri Hirata, Atsuro Yokoyama, Tsukasa Akasaka, Motohiro Uo, Makoto Matsuoka, Noriyuki Takashi, Yasunori Totsuka, Kosuke Ishikawa, Sachiko Ito, Yasutaka Yawaka: International Symposium on "Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes" (ISNT2008), Sapporo, June 16-17, 2008

Carbridization and Nitrization of Ta and Ti for the improvement of wearresistance of implants, F. Watari, YH Zhu, M. Uo, 21th Annual Meeting of the Society for Titanium Alloys in Dentistry, Tokushima, Feb 15-16, 2008

The application of X-ray scanning analytical microscope (XSAM) for the analysis of biological and dental specimens, M. Uo, A. Yokoyama, F. Watari, 9th International Conference on X-ray Microscopy, Zurich, July 21-25, 2008

Multi-wall Carbon Nanotubes Monolith prepared by Spark Plasma Sintering (SPS) and its mechanical property, M. Uo, T. Akasaka, I. Tanaka, F. Munekane, M. Omori, H. Kimura, F. Watari, International Symposium on "Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes" (ISNT2008), Sapporo, June 16-17, 2008

Properties and cytotoxicity of metal encapsulating carbon nanocapsules, M. Uo, The annual meeting of the Japanese society of metals: Materials strategy session 2, Mar. 28, 2008

Preparation and mechanical properties of fiber reinforced resin with silk, M. Uo, S.

Abe, T. Akasaka, F. Watari, the 51th General Session of the Japanese Society for Dental Materials and Devices, Yokohama, Apr.26-27, 2008

Micro XAFS analysis of metal containing biological specimens using X-ray polycapillary optics, M. Uo, K. Asakura, 11th XAFS conference, Himeji, Sept. 6-9, 2008

Development of flowable composite resin using the flake shaped glass filler, M. Uo, F. Watari, J. Ino, the 52th General Session of the Japanese Society for Dental Materials and Devices, Osaka, Sep.20-21, 2008

Development of flowable composite resin using the flake shaped glass filler, M. Uo, S. Abe, T. Akasaka, F. Watari, the 52th General Session of the Japanese Society for Dental Materials and Devices, Osaka, Sep.20-21, 2008

Culture of osteoblastic cells on transparent conductive thin films of single-wall carbon nanotubes; T. Akasaka, A. Yokoyama, M. Matsuoka, S. Abe, M. Uo, T.Hashimoto, F. Watari: the 20th Congress of Society for Organ Substitution and Regeneration Medicine, Sapporo, Feb.2, 2008

Culture of osteoblast-like cells on transparent conductive thin films with carbon nanotubes; T. Akasaka, A. Yokoyama, M. Matsuoka, S. Abe, M. Uo, Y. Sato, K. Tohji, T. Hashimoto, F. Watari, the 34th the Fullerenes and Nanotubes General Symposium, Nagoya, Mar.3-5, 2008

Culture of osteoblast-like cells on transparent conductive single-walled carbon nanotubes thin films; T. Akasaka, S. Abe, M. Uo, F.Watari: the 51th General Session of the Japanese Society for Dental Materials and Devices, Yokohama, Apr.26-27, 2008

Cell culture on transparent conductive thin films with single-walled carbon nanotubes; T. Akasaka, S. Abe, M. Uo, F. Watari: the 52th General Session of the Japanese Society for Dental Materials and Devices, Osaka, Sep.20-21, 2008

Effect of carbon nanotubes thin films on cell morphology and migration; T.AKASAKA, M.Matsuoka, F.Watari; the 212th Meeting of the Electrochemical Society, Hawaii, Oct.12-17, 2008

Biodistribution of organic/inorganic particles; Shigeaki Abe, Chika Koyama, Mitsue Esaki, Iosif D. Rosca, Tsukasa Akasaka, Motohiro Uo, Manabu Morita, Yoshinori Kuboki and Fumio Watari, 20th annual meeting of Society for Organ Substitution and Regenaration Medicine, Feb. 2, 2008

Imaging of exposed particulate materials in mice; Shigeaki Abe, Mitsue Esaki, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki and Fumio Watari, 51st The Japanese Society of Dental Materials and Devices, Yokohama, Apl. 26-27, 2008

Distribution imaging of organic/inorganic micro particle; Shigeaki Abe, Chika Koyama, Mitsue Esaki, Iosif Rosca, Tsukasa Akasaka, Motohiro Uo, Manabu Morita, Yoshinori Kuboki and Fumio Watari, 51st annual meeting of japan society of microscopy, Kyoto, May 21-23, 2008

Determination of administered organic/inorganic particles in mice; Shigeaki Abe, Chika Koyama, Mitsue Esaki, Ikuhiro Kida, Iosif Rosca, Tsukasa Akasaka, Motohiro Uo, Manabu Morita, Yoshinori Sato, Balachandran Jeyadevan, Yoshinori Kuboki, Kazuyuki Tohji, Fumio Watari, 8th World Biomaterial Congress 2008, , May 28 - Jun. 1, 2008

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Distribution imaging of mangetic particles in mice compared with magnetic resonance imaging and X-ray scanning analytical microscope; Mitsue Esaki, Shigeaki Abe, Tsukasa Akasaka, Motohiro Uo, Toshiaki Hosono, Yoshinori Sato, Balachandran Jeyadevan, Yoshinori Kuboki, Manabu Morita, Kazuyuki Tohji, and Fumio Watari, International Symposium on "Nanotoxicology Assessment and

Biomedical Application of Fine Particles and Nanotubes", Sapporo, Jun. 16-17, 2008

A DFT and MD study on the interaction of carbon nano-materials with metal ions; Shigeaki Abe, Fumio Watari and Hiroto Tachikawa, International Symposium on Multi-scale Simulationsof Biological and Soft Materials (MSBSM2008), Tokyo, Jun. 19, 2008

Controlled calcification with bio-mimetic polymer; Tomoki Ishida, Shigeaki Abe, Tsukasa Akasaka, Motohiro Uo, and Fumio Watari, 52nd The Japanese Society of Dental Materials and Devices, Suita, Sep. 20-21, 2008

A DFT and MD study on the interaction of carbon nano-materials with metal ions; Shigeaki Abe, Fumio Watari, Tomoya Takada, and Hiroto Tachikawa, 2nd annual meeting of japan society for molecular science, Fukuoka, Sep. 24-27, 2008

Biodistribution of several inorganic micro/nano particles in mice; Shigeaki Abe, Chika Koyama, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki, and Fumio Watari, 21st International Symposium on Ceramics in Medicine (Bioceramics21), Buzios, Oct. 21-24, 2008

Internal distribution behavior of inorganic particles in mice; Shigeaki Abe, Tetsu Yonezawa, Chika Koyama, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki, and Fumio Watari, 21st International symposium of microprocesses and nanotechnology, Fukuoka, Oct. 27-30, 2008

A DFT and MD study on the evaporation dinamics of water molecules on carbon nano-materials; Shigeaki Abe, Yoshinori Nagoya, Fumio Watari and Hiroto Tachikawa, 8th International Conference on Nano-Molecular Electronics, Kobe, Dec. 16-18, 2008

Cell adhesion to CNT coated silicone rubber; M. Matsuoka, T. Akasaka, T. Hashimoto, Y. Totsuka, F. Watari; International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun.

16-18, 2008

The development of reconstruction materials having both high cellular adhesiveness and electric conductivity; M. Matsuoka T. Akasaka Y. Totsuka F. Watari, The 52nd General Session of the Japanese Society for Dental Materials and Devices, Suita, Sep. 20-21, 2008

Cell proliferation on flexible and electroconductive CNT coated silicone rubber; M. Matsuoka T. Akasaka Y. Totsuka F. Watari, Joint international meeting: 214th Meeting of ECS — The Electrochemical Society, 2008 Fall Meeting of The Electrochemical Society of Japan, Honolulu, Oct. 12-17

Cell culture on an imogolite scaffold, K. Ishikawa, M. Kaga, T. Akasaka, Y. Yawaka, M. Suzuki, F. Watari, International symposium on nanotoxicology assessment and biomedical, environmental application of fine particles and nanotubes, Sapporo, June 2008

Application of almino-silicate nanotubes, imogolite, to cell culture, K. Ishikawa, T. Akasaka, Y. Yawaka, F. Watari, The 52th general session of the Japanese society of dental materials and devices, Osaka, Sep, 2008

Development of multi walled carbon nanotubes coated collagen for cell cultureing, Michiko Terada, Motohiro Uo, Yoshimasa Kitagawa, Fumio Watari; International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

3D scaffold with carbon nanotube coated collagen sponge; Eri Hirata, Motohiro Uo, Hiroko Takita, Tsukasa Akasaka, Fumio Watari, Atsuro Yokoyama, 86th General Session & Exibition of the IADR. Tronto, Canada. July. 2008

Multiwalled carbon nanotube coating of 3D cell culture scaffold: E.Hirata, M.Uo, H.Takita, T.Akasaka, F.Watari, A.Yokoyama; International Symposium on"Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes" Sapporo, June. 2008

Application of carbon nanotube coated collagen sponge for 3D scaffold :E.HIRATA, M.UO, A.YOKOYAMA, F.WATARI; The Japanese Society of Dental Materials and Devices, Tokyo, April. 2008

The difference of the effect of multi-walled carbon nanotubes on human hepatic normal and cancer cells, Sachiko Ito, Yasutaka Yawaka, Tsukasa Akasaka, Fumio Watari, International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Distribution imaging of magnetic particles in mice compared with magnetic resonance imaging and X-ray scanning analytical microscope, Mitsue Esaki, Shigeaki Abe, Tsukasa Akasaka ,Motohiro Uo, Manabu Morita, Toshiaki Hosono, Yoshinori Sato, Balachandran Jeyadevan, Yoshinori Kuboki, Kazuyuki Tohji, Fumio Watari; International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Geometry of artifical ECM: Parallel inductions of bone and vasculature within the tunnels of honeycomb-shaped beta-tricalcium phosphate ceramics in vivo, Yoshinori Kuboki, Shouhei Iku, Michiko Terada, Yoshimasa Kitagawa, Mariko Takayama, Makiko Kono, Yu Aso, Tohru Kaku, Motohiro Uo, Fumio Watari, International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Low-voltage and high-voltage TEM observatiions on CNT of rat in vivo, N.Sakaguchi, F.Watari, A.Yokoyama, Y.Nodasaka, H.Ichinose, International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

: Geometric property of rod-like molecules: Interaction mechanism of collagen triple-helix with carbon nanotubes, Yoshinori Kuboki, Michiko Terada, Yoshimasa Kitagawa, Shigeaki Abe, Motohiro Uo, Fumio Watari, International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Microstructure and Surface Characteristics of Anodized and Hydrothermal Treated

Titanium, Il Song Park, Man Hyung Lee, Min Ho Lee, Kyeong Won Sel, Tae Sung Bae, Fumio Watari: International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Fabrication and influence of heat treatment on nano-structured titanium oxide, Madhav Prasad Neupane, Kim Yu Kyoung, Il Song Park, Min Ho Lee, Tae Sung Bae, Fumio Watari; International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Preparation of mono-dispersed carbon nanotubes for exposure and risk assessment exerimental studies, Bunshi Fugetsu, Fumio Watari, International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Maturation of osteoblast-like SaoS2 induced by carbon nanotubes, Xiaoming Li, Hong Gao, Motohiro Uo, Yoshinori Sato, Tsukasa Akasaka, Shigeaki Abe, Qingling Feng, Fuzhai Cui, Fumio Watari, International Symposium on Nanotoxicology Assessment and Biomedical, Environmental Application of Fine Particles and Nanotubes, Sapporo, Jun. 16-18, 2008

Facilities and Capabilities

XSAM: HORIBA XGT-2000V, Scanning X-ray analytical microscope for elemental mapping analysis
XRD: Rigaku Multiflwx, X-ray diffractometer (3kVA)
AFM: TopoMetrix TMX2000 Explorer, AFM for dry and wet specimens
NSOM: TopoMetrix Aurora, Near field Scanning Optical Microscope
Laser Raman Spectrometer: Dilor Labram, Laser Raman Spectrometer with mapping analysis
ICP: HITACHI P-4010, ICP emission spectrometer for analysis of elements in aquaous solution

FT/IR: Jasco FT/IR-300E, FT/IR spectrometer with microscopic IR measurement
Particle Size Analyzer: Shimadzu SALD-7000, Particle size distribution analysis with laser scattering
Surface Area Analyzer: Shumadzu, Surface area analysis with gas absorption/desorption
Universal Testing Machine: INSTRON MODEL 4204, Testing for mechanical properties of materials
Laser Welder: ATJ TLL7000, Nd-YAG pulse laser welder with computer controlled x-y stage
Cold Isostatic Press: Hiikari Koatsu Kiki (10000atm type and 20000atm type)
:Kobelco, Large volume isostatic press (4000atm)
Vickers Hardness Tester: Shimadzu
Acoustic Emission: Physical Acoustic Corporation
Thermal Gravitometry and Differential Thermal Analysis (TG/DTA): Rigaku Denki
Diamond Cutter: Buehler and Struers diamond cutter

LABORATORY OF ADVANCED HIGH-TEMPERATUER MATERIALS

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The research activities of the laboratory are directed toward study and development of the advanced high strengthened ODS alloys and high temperature corrosion, oxidation and protection of metals.

(1) Nano-meso structure control of 9Cr-ODS ferritic steels

Structure of the 9Cr-ODS ferritic steels can be successfully controlled by the $\alpha-\gamma$ phase transformation, and their high-temperature creep strength is the most superior worldwide in the class of ferritic tubes. This is owing to existence of the residual ferrite phase within the tempered martensite phase. In our group, the formation mechanism of the residual ferrite and the origins its strength are intensively investigated through synthesizing ODS alloys by ball-milling and their analyses by means of nano-indentation measurement, differential thermal analysis, high-temperature X-ray diffraction, SEM and TEM observation.

It was clearly revealed that the ferrite is able to remain over Ac3 point by pinning of the $\alpha-\gamma$ interface due to nano-size oxide particles; this ferrite is a non-equilibrium phase, and designated as residual ferrite. This phase is composed of so-called ultrafine grains with size of 500 nm. Therefore, grain refinement strengthening can be effectively performed in the residual ferrite phase, which is the real origin for the superior high-temperature strength of the 9Cr-ODS ferritic steels.

(2) Texture control of 12Cr-ODS ferritic steels

The appropriate cold-rolling and heat-treatment processes are being investigated for the manufacture of 12Cr-ODS ferritic steels, focusing on the texture development. A measurement technique by FE-SEM/EBSP (Electron Back Scattering Pattern) is mainly applied in this study. Cold-rolling of the sheet induces strong $\alpha-$fiber texturing composed of {111}～{001}<110> parallel to the rolling direction and rolling plane. Recrystallization of the cold-rolled sheet takes place at elevated temperatures beyond 1100 ℃. The formation mechanism of the recrystallized texture, typically {011}<001>, was investigated; this unique texture was revealed to exist within shear bands of the cold-rolled structure. This finding suggests that the recrystallized grains are nucleated during the stage of cold-rolling, and are selectively grown at temperatures beyond 1100℃.

(3) Development of Ni-based, Co-based and Nb-based ODS superalloys

Basic study for development of the Ni based ODS superalloys is being conducted. It was found that mechanical alloying (MA) induces nano-crystal formation of in 50 nm size in the Ni-Y_2O_3 system, and the nano-size grains are maintained up to 1300℃. Beyond this temperature, recrystallization and grain-growth takes place due to coarsening of Y_2O_3 oxide particles. A study for making extremely fine distributions of oxide particles is being also conducted; the effective elements for fine oxide particle distribution were discovered and a patent application was conducted. In addition, effects of MA on γ' (Ni_3Al) precipitation and growth in the Ni-Al-Y_2O_3 system and more practical alloys (MA6000) were investigated. Co-based ODS alloys was investigated from a viewpoint of fine distribution of oxide particle by addition of particular elements. Development of Nb-based ODS alloy was started in the system of Nb-50Al, Nb-15Al and Nb-7Al.

(4) Water vapor effects on the high temperature oxidation of Ni-based alloy

The effects of water vapor on the oxidation of Pt-modified γ'-Ni-25at%Al alloys are being investigated. Water vapor decreased the initial oxidation mass gain on the exclusive Al_2O_3 forming alloys. No significant difference of the microstructure of oxide scale was found for the alloys oxidized in dry and wet atmospheres. α-Al_2O_3 grains formed at the scale/alloy interfac, and it occurred earlier in wet condition.

(5) Phase transformation behavior of Al_2O_3 scale during high temperature oxidation

Very thin (~50nm) Fe, Cr, or Ti coating on NiAl or FeAl alloys was found to suppress formation of metastable Al_2O_3, α-Al_2O_3 scale formed from the initial stage of oxidation, and the growth rate of coated alloy decreased significantly. This direct formation of α-Al_2O_3 scale was explained by the “sympathetic nucleation” of α-Al_2O_3 scale from the corundum crystal of Fe_2O_3 or Ti_2O_3. Those elements were also found to accelerate the phase transformation to α-Al_2O_3 when the element was coated on pre-formed metastable Al_2O_3 scale. Ni was found to retard the phae transformation to α-Al_2O_3 scale.

(6) Effect of alloying elements on internal oxidation of Nb-Al alloys

Growth kinetics of internal oxide of Al_2O_3 in the Nb_3Al intermetallic compound decreased when Re, Mo, or Ta was added into Nb_3Al substrate. Effect of those elements on oxygen solubility is now under investigating.

(7) Effects of impurity elements on the spallation behavior of low-C steel

Scale spallation behavior was investigated on the low-C hot rolled steels with different contents of P. Oxide scale was easily spalled off on the steels with P, when the oxidation was conducted above 1150°C. P-rich oxide scale was found at the scale/steel interface, resulted in the formation of liquid phase at the interface.

Presentations

Decomposition and precipitation behavior of oxide particles in nano-Ni crystals; T. Hoshino, S. Hayashi and S. Ukai: ISIJ and Jpn, Inst. Metals joint meeting, Jan. 2008.

Formation mechanism of ultra-fine grains in 9Cr-ODS steels: N. Chikata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: ISIJ and Jpn, Inst. Metals joint meeting, Jan. 2008.

Texture formation in 12Cr-ODS steels by recrystallization: H. Numata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: ISIJ and Jpn, Inst. Metals joint meeting, Jan. 2008.

Nano-mesoscopic structure and strength mechanism of 9Cr-ODS serritic steels: S. Ukai, N. Chikada, M. Yamamoto, S. Hayashi, S. Ohnuki, T. Kaito and S. Ohtsuka: International Symposium on Materials Design for Infrastructures, Graduate School of Engineering, Hokkaido University, Sapporo Japan, March 3 - 4, 2008

Decomposition and precipitation of oxide particles in nano-Ni crystals by mechanical alloying; T. Hoshino, S. Hayashi and S. Ukai: Jpn, Inst. Metals, March, 2008.

Formation of ultra-fine grains in 9Cr-ODS steels: N. Chikata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: Jpn, Inst. Metals, March, 2008.

Texture formation in ODS steels by cold-rolling and recrystallization: H. Numata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: Jpn, Inst. Metals, March, 2008.

Formation of ultra-fine grains and high-temperature strength in ODS steels: N. Chikata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: ISIJ and Jpn, Inst. Metals joint meeting, July. 2008.

Residual ferrite formation in 9Cr-ODS steels: M. Yamamoto, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: Inst. Metals joint meeting, July. 2008.

γ' precipitation in mechanical alloyed Ni-Al alloy: A. Minami, Hayashi and S. Ukai: Jpn, Inst. Metals joint meeting, July. 2008.

Formation of ultra-fine grains and high-temperature strength in ODS steels: N. Chikata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: Jpn, Inst. Metals, Sep. 2008.

Residual ferrite formation in 9Cr-ODS steels: M. Yamamoto, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: Jpn, Inst. Metals, Sep. 2008.

Formation mechanism of recrystallization texture in 12Cr-ODS steels: H. Numata, S. Hayashi, S. Ukai, S. Ohtsuka and T. Kaito: Jpn, Inst. Metals, Sep. 2008.

Precipitation and growth of γ' precipitates in Ni-15 at% Al by mechanical alloying: A. Minami, Hayashi and S. Ukai: Jpn, Inst. Metals, Sep. 2008.

Effects of added elements on fine distribution of oxide particles in Ni-based ODS superalloys: T. Hoshino, S. Hayashi and S. Ukai: Jpn, Inst. Metals, Sep. 2008.

Formation of Ultrafine Grains in 9Cr-ODS Ferritic Steel: N. Chikata, S. Hayashi, S. Ukai, S.Ohnuki, S. Ohtsuka and T. Kaito: International Conference on Heat Treatment and Surface Engineering, Kobe, October 27-30, 2008

Decomposition-Precipitation Behavior of Oxide Particles in Ni nano-Crystals: T. Hoshino, S. Hayashi and S. Ukai: International Conference on Heat Treatment and Surface Engineering, Kobe, October 27-30, 2008

The effect of water vapor on the oxidation of pure-Ni: M. Auchi, S. Hayashi, T. Narita, and S. Ukai: Fall meeting of JSCE 2008, Nagasaki University, Nagasaki, September 17-19, 2008.

Oxidation behavior of Fe-Cr-Al alloy at 700 and 900°C: D. Igarashi, S. Hayashi, and S. Ukai: Fall meeting of JSCE 2008, Nagasaki University, Nagasaki, September 17-19, 2008.

Fracture behavior of Al_2O_3 scale formed on oxidation resistant coating on Hastelloy-X alloy under creep deformation: S. Takagi, S. Hayashi, T. Narita, and S. Ukai: Fall meeting of JSCE 2008, Nagasaki University, Nagasaki, September 17-19, 2008.

Metastable to stable Al_2O_3 phase transformation behavior formed on FeAl alloy with various elements coating: Y. Kitajima, T. Nishimoto, S. Hayashi, T. Narita, and S. Ukai, Fall meeting of JSCE 2008, Nagasaki University, Nagasaki, September 17-19, 2008.

The Effect of Additional Elements on Oxide Scale Evolution of Fe-20%at.Cr-10at.%Al alloy at 900℃ in air: Y. Kitajima, S. Hayashi, S. Ukai, and T. Narita: 7th Internatonal Symposium on HTCP 2008, Les Embiez, France, May 18-23, 2008.

Creep Deformation / Oxidation Behavior of Re-Cr-Ni Diffusion Barrier Coated Hasetelloy-X at 970℃ in Air: S. Hayashi, M. Sakata, S. Ukai, and T. Narita, 7th Internatonal Symposium on HTCP 2008, Les Embiez, France, May 18-23, 2008.

The Effect of Water Vapor on the Oxidation of Pt-modified Ni-22Al alloys: S. Hayashi, M. Auchi, T. Narita, and B. Gleeson, 4th IMR Symposium on HTCP, Shenyang, China, Septemper 23-26, 2008.

Oxidation of Pt-modified γ–γ' alloys and coatings from a chemical potential and fiffusion perspective: S. Hayashi and B. Gleeson, NIMS WEEK 2008, Materials Science for Highly Efficient Use of Energy and Resources, Tsukuba, July 14-18, 2008.

LABORATORY OF SPECIALLY PROMOTED RESEARCH

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The research activities of the laboratory of Specially Promoted Research, (2006-2010), supported by Japanese Government, are focusing on 1) elucidating of the interaction between various alloys (superalloys, Ni-based alloys and Fe-based alloys) and coatings,2) understanding high temperature oxidation and corrosion behavior of alloys and coatings,3) comprehending the influence of coatings on mechanical properties,4) developing a novel diffusion barrier system to improve high temperature capabilities. Furthermore we are aiming to transfer our research successes to the practical uses, such as gas turbines and jet engines.

Current topics on research are in the following:

(1)Formation of oxidation resistant coating with diffusion barrier

A new bond-coat with a duplex layer structure, an inner σ-（Re,W,Ni,Cr）as a diffusion barrier and an outer Ni-aluminide as Al reservoir, was formed on superalloys, Ni-based alloys and Fe-based alloys(e.g.TMS-138, Hastelloy X and SUS301). Diffusion barrier layer was produced by Re-Ni and Ni-W electroplating from aqueous solutions followed by Cr pack cementation at high temperatures. Al reservoir layer was formed by Ni electroplating, followed by Al pack cementation.

(2)Oxidation behavior of coatings with the diffusion barrier

Oxidation behavior of the coating with diffusion barrier was examined by oxidation testing carried out at temperature between 1323 and 1423K. It was found that σ–(Re,W,Ni,Cr) act as a diffusion barrier from both inward diffusion of Al and outward diffusion of alloying elements in the alloys substrate.

(3)Inter-diffusion of Pt into superalloys

Inter-diffusion of Pt into Ni-based superalloys was investigated. 5μm of Pt layer was electroplated on superalloy substrate then they were heat-treated at 1273K for up to 100h in vacuum. Samples were cross-sectioned and prepared for analysis using an Ar ion cross-polisher, and then imaged by SEM or FIB. Cross-sections were chemically analyzed by EPMA.

(4)Effect of titanium on the suppression of meta-stable alumina formation

The effect of titanium on the suppression of meta-stable alumina formation on alumina-former alloys (Ni-Al and Ti-Al) was investigated. To suppress the rapid growth of meta-stable alumina phases at 1073-1173K, a thin layer of titanium was deposited on the NiAl alloy. Oxide surface morphology and XRD revealed that uncoated NiAl alloy formed needle-like gamma or theta alumina at 1173 K, However, no indication of whiskers on the surface of Ti coated NiAl.

Presentations

T. Narita, T. Yoshioka, T. Nishimoto, T. Izumi, S. Ford, S. Hayashi; Concept and Formation of Diffusion Barrier Coating System on High-Temperature Alloys and Its oxidation Behavior, Turbine Forum 2008, Advanced Coatings for High Temperatures, April 23-25 (2008), Nice, France.

T. Narita; Formation of Pt-modified γ'-Ni_3Al and Re-base Alloy Coatings and Cyclic Oxidation Behavior of Coated Superalloy (Key-note lecture), High Temperature Corrosion and Protection of Materials 2008, May 18-23(2008), Les Embiez France.

T. Narita: Diffusion Barrier Coating Systems to Realize High Performance Gas Turbines - Compatibility between Anti-Oxidation and Mechanical Properties- (Plenary lecture), The 13th National Symposium on Power and Energy Systems (SPES 2008), pp. 15-22, June, 2008. Sapporo Japan

T. Narita: Diffusion Barrier Coating System and Oxidation Behavior of Coated Alloys (Invited lecture), 4th IMR Symposium on Materials Sciences and Engineering, Sep. 23-26 (2008) Shenyang China

T. Narita; Diffusion Barrier Coating System and Oxidation Behavior of Coated Alloys (Invited lecture), 214th ECS Meeting –Honolulu, HI, October 12-17(2008), Hawaii, USA

S. Saito, K. Kurokawa, S. Hayashi, T. Takashima, and T. Narita; Tie-lined Compositions of the σ and (γ, γ', β) phases in a Ni-Al-Re-Cr-System at 1423K, 214th ECS Meeting –Honolulu, HI, October 12-17(2008), Hawaii, USA

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Our group has intended to explore the fundamental corrosion mechanism of metals, development of corrosion monitoring system, surface finishing of aluminum and magnesium alloys, corrosion-related phenomena in fuel cell, and numerical simulation of adatom on metals in plating process.
Current topics on research are in the following:

(1) Development of a new pH sensor using porous aluminum anodic oxide film.

A porous anodic oxide film formed on Al was developed as a new pH-sensitive film. A porous anodic oxide film was immersed in an aqueous solution containing pH indicator reagents and boiled to seal them in the film. Litmus, bromthymol blue (BTB), and Congo red were used as pH indicator reagents. The film containing litmus changed its color reversibly within 1 s as a function of the test solution pH. The film showed superior durability in the solution at pH of 1 - 12 because of a stable boehmite layer covering the surface within that range. From the response of color change as a function of sealing time, it was inferred that the color change occurred mostly at the film's surface region. Optimization of film thickness, the choice of pH indicator reagent, and sealing condition are important to prepare a highly pH-sensitive film. Optical pH-sensor was manufactured using BTB sealed film and optical fibre and it was confirmed that light absorbance at specific wavelength changed continuously in a wide pH range.

(2) Development of a new surface coating method for Mg alloy.

The deposition of stannate chemical conversion coatings on AZ91 D magnesium alloy by using the potentiostatic technique was investigated to improve uniformity and corrosion protection performance of the coating film. It was found that anodic polarization during the stannate conversion process accelerated dissolution of magnesium ions and promoted deposition of the coating film. Optimal polarization potential was explored as a function of corrosion protection performance evaluated by potentiodynamic polarization curves in borate buffer solution. Scanning electron microscope observation and electrochemical corrosion tests of the stannate-coated samples confirmed significant improvement in uniformity and corrosion resistance of coatings deposited by the potentiostatic technique compared to those of coatings deposited by the simple immersion method. The pH and temperature of a stannate bath was optimized to obtain superior quality of coatings. Another coating technique was also developed in which electroless nickel-phosphorus film was plated on AZ91 D magnesium alloy prepared with molybdate chemical conversion coatings to obtain pore free-and highly adhesive corrosion protective coating.

(3) Size effect of electrodes in plating process on Al alloy.

In fabrication of LSI, electroless Ni plating is applied to bonding pad composed of Al-Si alloys. In this process it is known that the quality of plating film depends on the size of pads. To clarify the property and origin of this "size effect" in plating process, multiple electrode system was applied to double zincate pretreatment process and electroless Ni-P plating process of Al specimen. Various size of Al specimens were embedded in epoxy region and connected to electric circuit to detect coupling current between these specimens. Depending on the size and shape of specimen, anodic or cathodic coupling current was observed during the double zincate process and plating process. This size effect was interpreted in a term of critical size of electrode which can be divided into anode or cathode area.

(4) Application of multichannel electrode method to crevice corrosion.

Crevice corrosion of iron was evaluated using multichannel electrodes method in which ten individual working electrodes of pure iron were embedded in resin, placed in a artificial crevice, and immersed in NaCl solution. The WEs were connected to electronic circuit which allowed galvanic coupling between them and measurement of their individual coupling current or open circuit potential. Time-transient of spatial distribution of coupling current and open circuit potential showed sequential transition of coupling current on WEs at the middle position of crevice from cathode to anode. The transition was explained by the change in pH and concentration of dissolved oxygen in the crevice, and related to introduction and consumption of dissolved oxygen in the crevice solution, and circulation of gap solution from / to the outside of the crevice.

(5) Corrosion measurement of metals used in saltery plant using multichannel electrodes method

Saltery plant is running under highly corrosive condition, i.e., aqueous environment containing saturated sodium chloride at high temperature more than 100 celsius degree. Corrosion monitoring system for saltery plant under operation condition was thus developed using multichannel electrode system, and applied it to the crevice corrosion of SUS316L, NAS64, NAS185N and NAS254N stainless steels. The specimen was constructed from five sheets of these stainless steels, wired, insulated, piled and embedded in epoxy resin. Small hole was made through five sheets to reproduce the crevice condition. These stainless sheets were connected to electronic circuit which enables measurement of participating current on individual electrode under the coupling condition. Using this system, distribution of coupling current as a function of depth in the artificial crevice, kinds of stainless steel, and oxygen concentration was evaluated.

(6) Corrosion monitoring of thin copper film in high temperature solution using resistometry.

Radiative nuclear wastes produced in power plant is considered to be stored deep-underground to separate them from civil environment. Various kinds of metals have been evaluated to build a overpack container of such nuclear wastes in a glassified form. In order to evaluate corrosion rate of copper in repository condition, resistometry method was applied to thin copper film with thickness of 5 μm. A couple of Cu films was sealed in laminate film, and one of them was exposed to electrolyte solution containing various kinds of ions contained in underground water kept at 80 celsius degree. Relative resistance change of corroding film to non-exposed film was recorded to compensate influence of temperature change, and corrosion rate of Cu film was evaluate from resistance change as a function of ion species and dissolved oxygen concentration in the solution. Corrosion was accelerated in the solution containing sulfide ions or ammonium ions, while acceleration of corrosion due to sulfide ions was suppressed by pre-injected carbonate ions to the solution.

Presentations

Monitoring of crevice corrosion of stainless steels used in saltery plant; K. Azumi : Joint int. meeting 214th meeting of ECS and 2008 fall meeting of the electrochem. soc. japan, Honolulu, Hawaii, Oct., 2008.

Electroless Ni-P deposition on AZ91D magnesium alloy prepared by molybdate chemical conversion coatings; H. H. Elsentriecy and K. Azumi: *ibid.*

Depassivation pH of austenitic stainless steels in NaCl aqueous solution; K. Fushimi, K. Takakura, H. Habazaki, H. Konno, K. Azumi, and S. Tsuri: *ibid.*

Corrosion measurement of metals used in saltely plant using multichannel electrodes method; K. Azumi: The 20th meeting of research grand by the salt science research fundation, Tokyo, July, 2008.

Development of pH sensitive film using porous anodic oxide film of Al; F. Nishiyama, H. Konno, and K. Azumi: AST2008, Rusutsu, Sept., 2008.

Corrosion monitoring of copper film using thin film resistometry; K. Azumi: Annual meeting of Corrosion Society on Japan, 2008, Omiya, May, 2008.

Improvement in stannate chemical conversion coatings on AZ91 D magnesium alloy using the potentiostatic technique; H. H. Elsentriecy, H. Konno, K. Azumi: *ibid.*

Effect of gravity on crevice corrosion of iron; A. Naganuma, K. Azumi, and H. Konno: The 117th Annual Meeting of Surf. Finish. Soc. Jpn., Tsudanuma, Oct., 2008.

Development and characterization of pH sensitive film using porous Al oxide film; F. Nishiyama, K. Azumi, and H. Konno: *ibid.*

Development of pH sensitive film using porous Al oxide film; F. Nishiyama, K. Azumi, and H. Konno: Winter Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2008.

Analysis of growth factors of CNT on Fe nano-particle catalysis using CVD method; J. Kanno, K. Azumi, H. Konno: *ibid.*

Al plating on Mg from molten-salt bath; A. Sasaki, M. Ueda, K. Azumi, and H. Konno: The Joint Meeting of the Hokkaido Secs. of Electrochem. Soc. Jpn., Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, Jan., 2008.

Development of new electroless Ni plating method on Al-Si alloys and evaluation of its adhesion strength; S. Egoshi, K. Azumi, and H. Konno: *ibid.*

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Prof. Ryosuke O. Suzuki was nominated as the professor of the laboratory, and he merged from Kyoto University on March 2006. He began to study the non-ferrous metallurgy based on the molten salt electrolysis. In April 2009, Assoc. Prof. Dr. Yoshiaki Kashiwaya shifted to Kyoto, Japan, and re-started to work in the ferrous metallurgy as Associated Professor at Department of Energy Science and Technology, Kyoto University. The laboratory is currently seeking for the associate professor. Dr. Hiroshi Kinoshita works using the transmission electron microscopies for the radiation damage analysis.

The research activities of the laboratory lead by Prof. Suzuki are directed to design the economical and environment-friendly processes for materials especially at high temperatures. The wide variety of researching approach is introduced such as molten salt electrolysis, the heat treatment in the ambient pressure of non-equilibrium gas, thermoelectric phenomenon, etc. The extraction metallurgy of the refractory metals such as niobium and tantalum, and of valve metals such as titanium, vanadium and zirconium, contains many interesting topics when the molten electrolysis of $CaCl_2$ is applied. The non-equilibrium gases such as ozone and nitrogen radical are also attractive in the field for oxide and nitride coating. The thermoelectric power generation is designed from the view of material design and heat exchange between two thermal fluids.

Current topics on research are in the following:

(1) Molten salt electrolysis of $CaCl_2$

Reduction of the oxides of titanium, vanadium, niobium and tantalum are studied when the CaO dissolved in the molten $CaCl_2$ is electrochemically decomposed to form metallic calcium. A low oxygen potential can form the metallic powders at the cathode. The reduced metallic powder is prepared directly from the oxides as well as CaO. The homogeneous metallic alloy powder can be synthesized from the oxide mixture using the same method. The mechanism of this proposal is examined from the electrochemistry and thermodynamics using the evolved gas analysis.

(2) Non-equilibrium gas treatment

Pure nitrogen gas is introduced in the field applying a RF high voltage and it is successfully discharged. The non-equilibrium gas atmosphere extracted from the field is highly activated and it plays such as nitrogen radicals or N_3 gas. It reacts with the metallic surfaces to form the corresponding nitrides such as Fe_4N, which does not form in an ambient atmosphere of pure nitrogen.

Other activities

(3) Thermoelectric power generation

An optimization of the thermoelectric power generation is mathematically designed to generate the maximum output. The heat exchange between the two fluids is optimized to give the largest temperature difference along the large thermoelectric panels.

(4) Copper removal from the iron scrap

Using the analogy with the copper smelting, we plan that the impurity copper in molten steel will be removed as the copper sulfide when a high sulfur potential can be applied to the iron scrap. Some carbonates are served to remove copper from the iron-containing sulfide liquid.

Prof. R.O. Suzuki was invited at the International Round Table on Titanium Production in Molten Salts which was held at Köln, Germany, March 2008. He presented a lecture on the electrolysis of CaO and simultaneous reduction of TiO_2 in the molten $CaCl_2$. After the conference, he visited the Swiss Federal Institute of Technology Zürich (ETHZ) and presented an invited lecture on the thermoelectric power generation. He visited there again on September 2008 and presented the invited lecture on the electrolysis of TiO_2 in the molten $CaCl_2$. October 2008, he presented the calciothermic reduction of $TiCl_4$ at the Intern. Symp. of Molten Salt and Ionic Liquids 16 (MS16), as a part of the annual meeting of the Electrochemical Society (ECS) at Hawaii, USA. Next week at the international joint symposium on Molten Salt (MS8), Kobe, he talked on the Ti particle formation from $TiCl_4$ in the molten $CaCl_2$.

The following foreign scientists visited this laboratory: Prof. Geir Martin Haarberg and Dr. Ole S. Kjos, Norwegian University of Science and Technology, Trondheim, Norway, Prof. Sommai Pivsa-Art, President Numyoot Songthanapitak, Vice President Churairat Duangdruen, Prof. It-arun Pitimon, Prof. Warunce Ariyawiriyanan, Dr. Watcharapong Worrasettapong, Dr. Teera Ngamsuntikul, Rajamangala University of Technology, Thanyaburi, Thailand, Prof. Yang Lun, Prof.Shao Xuemin, Prof. Yinfa Tao, Prof. Daniel He and Vice President Prof. Yanxin Wang, China University of Geosciences, Wuhan, China.

Presentations

Electrolysis and Reduction of Titanium Oxides in the Molten Salt of

($CaCl_2$+CaO) ; K. Kobayashi, Y. Oka and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan. 2008.

Dissolution of CO_2 gas into the Molten Salt of ($CaCl_2$+CaO/$CaCO_3$) ; J. Hashizume, Y. Oka and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan. 2008.

Reduction and Synthesis of Ti-6Al-4V alloy by the Molten Salt Electrolysis of ($CaCl_2$+CaO) ; H. Sakai, Y. Oka and R.O. Suzuki : The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Sapporo, Jan. 2008.

Reduction of Ti-6Al-4V by the Electrolysis of Molten ($CaCl_2$+CaO) ; H. Sakai, Y. Oka and R.O. Suzuki : The Annual Meeting of Iron and Steel Inst. Jpn., Tokyo, Mar. 2008.

Calciothermic Reduction and Simultaneous Electrolysis of CaO in the Molten $CaCl_2$−Some Modifications of OS Process ; R.O. Suzuki : 1st Intern. Round Table on Titanium Production in Molten Salts, Köln, Germany, Mar. 2008.

Thermoelectric Materials and Power Generation Using Two Thermal Fluids ; R.O. Suzuki : Besonderforschungsbericht am ETHZ Ceramik 2008, Zürich, Switzerland, Mar. 2008.

New Proposal to Metallic Titanium and its Alloys from TiO_2 ; R.O. Suzuki : Advances in Ceramic Science and Engineering 2008, Zürich, Switzerland, Sept. 2008.

Dissolution of CO_2 into the molten salt $CaCl_2$+CaO/$CaCO_3$; J. Hashizume, Y. Oka

and R.O. Suzuki : Annual Meeting of Jpn. Inst. Metals, Kumamoto, Sept. 2008.
Synthesis of Ti-6Al-4V Alloy Powder by the electrolysis of Molten $CaCl_2$+CaO ; H. Sakai, Y. Oka and R.O. Suzuki : Annual Meeting of Iron and Steel Inst. Jpn., Kumamoto, Sept. 2008.

Current density in OS Process for TiO_2 Reduction ; K. Kobayashi, Y. Oka and R.O. Suzuki : Annual Meeting of Jpn. Inst. Metals, Kumamoto, Sept. 2008.

Calciothermic Reduction of $TiCl_4$ Gas during the Electrolysis of $CaCl_2$ Melt ; R.O. Suzuki and T. Naito : Molten Salt and Ionic Liquids 16 (MS16), Pacific RIM Meeting on Electrochemical and Solid-State Science, Honolulu, HI, USA, Oct. 2008.

Direct Reduction of Liquid V_2O_5 in Molten $CaCl_2$; Y. Oka and R.O. Suzuki : Molten Salt and Ionic Liquids 16 (MS16), Pacific RIM Meeting on Electrochemical and Solid-State Science, Honolulu, HI, USA, Oct. 2008.

Calciothermic Reduction of $TiCl_4$ Gas by Electrolysis of CaO in $CaCl_2$ Melt ; R.O. Suzuki and T. Naito : Intern. Symp. of Molten Salt (MS8), Kobe, Oct. 2008.

Solubility of CO_2 gas in molten CaO-$CaCl_2$; J. Hashizume, Y. Oka and R.O. Suzuki : Intern. Symp. of Molten Salt (MS8), Kobe, Oct. 2008.

Synthesis of Ti-6Al-4V Alloy Powder by the electrolysis of Molten $CaCl_2$+CaO ; H. Sakai, Y. Oka and R.O. Suzuki : Intern. Symp. of Molten Salt (MS8), Kobe, Oct. 2008.

Current density in OS Process for TiO_2 Reduction ; K. Kobayashi, Y. Oka and R.O. Suzuki : Intern. Symp. of Molten Salt (MS8), Kobe, Oct. 2008.

Solubility of CO_2 gas in CaO-$CaCl_2$ melt ; J. Hashizume and R.O. Suzuki : 11th Symposium between Hokkaido Univ. and Univ. of Science and Technology Beijing, Sapporo, Nov. 2009.

Reduction of Oxides and Simultaneous Electrolysis of CaO in the Molten $CaCl_2$ (OS Process) ; R.O. Suzuki : 11th Symposium between Hokkaido Univ. and Univ. of Science and Technology Beijing, Sapporo, Nov. 2009.

Facilities and Capabilities

X-ray diffractmeter: Philips X'Pert Pro. A set for thin film XRD and powder XRD, and another set for high temperature XRD using Pt heating planer stage or Al_2O_3 crucible with RF heating. 127 detectors in a counting unit are able to measure more rapidly.
Oxygen and Nitrogen Analyzer: LECO TC-500. Inert gas extraction with carbon crucible and infrared absorption method. 20mass%-1 mass ppm.
Sulfur and Carbon Analyzer: LECO CS-444. Oxygen gas burning with RF heating and the converted CO_2 gas is detected by the infrared absorption method. 20mass%-1 mass ppm.
Themal Conductivity Measuring Unit: Kyoto Electrics. Hot disk method at room temperature.
CO/CO_2 Gas Analyzer: Yokogawa. In the range of 0.1vol% and 10vol%.
Constant voltage generators: Takasago Electrics. 4 sets. Max.50V and 20A.
High voltage amplifier: Takasago Electrics. 100V-8000V.
Ozone gas generators: max 8 and 3vol%O_3 gas in O_2 gas.
Thermal Analyzers: Shimazu TMA-50 and DTG-50. Pt heater to 1500C.
Hall coefficient mearsuring system: Toyo-Technica Regitest 8200.

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The research activities of our group are directed to an understanding of the mechanism of solid state reactions between ceramics and alloy, high temperature oxidation of carbides, and grain growth behavior of nano-grained oxides.

Current topics on research are in the following:

(1) Liquid-phase oxidation joining of yttria-stabilized zirconia and stainless alloy

Joining technique between Yttria-stabilized zirconia (YSZ) blocks via Al/stainless alloy/Al intermediate multilayers is developing as a sealing technique to maintain gas-tightness of planar solid oxide fuel cells (SOFCs) Almina layer, which was formed by oxidation of Al melt during joining process, is expected to act as protective layer for further oxidation of stainless alloy. Degradation of YSZ/stainless steel interface in oxidizing atmosphere is under investigation.

(2) Sol-gel HfO_2 coating on SiC polycrystal and its resistance to high temperature oxidation

Sol-gel HfO_2 coating process is developing to improve resistance to high temperature oxidation and corrosion of SiC. Coating of dense HfO_2 films on SiC polycrystal inhibited evaporation of SiO gas and CO gas from SiC. At present, coating process to prepare porous hafnia film on SiC polycrystal is investigating for environmental and thermal barrier coating.

(3) Grain growth behavior of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$. films prepared by a sol-gel process

Inhibition of the grain growth in cathode material, (La,Sr)CoO_3, is essential to extend the lifetime of solid oxide fuel cells (SOFC), because the grain growth causes higher overpotential in cathode, resulting in degradation in the SOFCs performance. Therefore, we investigated the grain growth behavior in $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) film with average grain size of 50 nm in various oxygen partial pressure to clarify the grain growth mechanism. Our results suggested that the grain growth was not controlled by the cation diffusion and should be controlled by transport of ions across the grain boundary.

Presentations

Effect of HfO_2 Coatings on High Temperature Oxidation Resistance of Sintered SiC Ceramics; M. Kasajima, T. Akashi, S. Shimada : The 46th Symposium on Basic Science of Ceramics, Basic Science Division, The Ceramic Society of Japan, Nagoya, Jan., 2008.

Active Oxidation Behavior of Sintered Silicon Carbide with Hafnia Coating; T. Akashi, M. Kasajima, H. Kiyono and S. Shimada : The 75th Meeting of Electrochemical Society of Japan, Kofu, Mar., 2008.

Bonding of Yttria-stabilized Zirconia via Al/Stainless Steel (SUS430)/Al interlayers; T. Akashi, T. Shimura and H. Kiyono : Joint Conference of The 2nd International Conference on Science and Technology for Advanced Ceramics (STAC2) and The 1st International Conference on Science and Technology of Solid Surface and Interface (STSI1), Chiba, May,2008.

Bonding of Yttria-stabilized Zirconia via Al/Stainless Steel/Al interlayers; T. Shimura, H. Kiyono and T. Akashi: Summer Meeting of Chemical Society of Japan, Hokkaido Branch, 2008, Kitami, Jul., 2008..

Interface Structure of Yttria-stabilized Zirconia Joined via Al/Stainless Steel/Al intermediate Multilayer; T. Akashi, T. Shimura and H. Kiyono: The 21st Fall Meeting of The Ceramic Society of Japan, Kita-Kyusyu, Sep., 2008.

Sol-Gel HfO_2 Coating on Sintered SiC Polycrystal as an Environmental Barrier Coating; T. Akashi, M. Kasajima and H. Kiyono: PRiME 2008 Meeting, The Electrochemical Society, Hawaii, HI, Oct., 2008.

Grain Growth Behavior of $La_{0.6}Sr_{0.4}O_{3-\delta}$ Film Dispersed with a Second Phase; T. Sawada and T. Akashi: PRiME 2008 Meeting, The Electrochemical Society, Hawaii, HI, Oct., 2008.

Effect of Oxygen Pressure on Grain Growth in $La_{0.6}Sr_{0.4}O_{3-\delta}$ Film Dispersed with a Second Phase; T. Sawada and T. Akashi: The 34th Symposium on Solid State Ionics of Japan, Tokyo, Dec., 2008.

Joning of Yttria-stabilized Zirconia via Al/Ni Alloy/Al Intermediate Multilayer; T. Akashi, T. Nukui and H. Kiyono: The IUMRS International Conference in Asia 2008, Nagoya, Dec., 2008.

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In April, Dr. Koji Fushimi promoted as an Associate Professor of Advanced Materials Chemistry Laboratory, which was directed by Prof. Hidetaka Konno. Our group has intended to explore the fundamental corrosion mechanism of metals and development of corrosion monitoring system and sensor devices using micro-electrochemistry.

Presentations (international symposia)

S. Hashizume, T. Nakayama, M. Sakairi, K. Fushimi; "Electrochemical Behavior of Low C•13%Cr Welded Joints by Using Solution Flow Type Micro-droplet Cell", NACE Corrosion 2008 Conference & Expo, Mar. 16-20, New Orleans, USA (2008).

S. Yamamoto, K. Fushimi, H. Habazaki, H. Konno; Diffusion limiting-current equation in the flowing-type droplet cell, AST2008, 2008.7.23-25, Rusutsu, Japan (2008).

T. Yamamoto, K. Fushimi, H. Habazaki, H. Konno; Repassivation behavior of Passive Film on Pure Iron in Borate Buffer Solution Investigated by Micro-indentation, AST2008, 2008.7.23-25, Rusutsu, Japan (2008).

M. Nakajima, Y. Miura, K. Fushimi, M. Takazawa, H. Habazaki; Spark Anodizing of Titanium and Its Alloys in Alkaline Aluminate Solution, AST2008, 2008.7.23-25, Rusutsu, Japan (2008).

M. Uemura, T. Yamamoto, Y. Aoki, K. Fushimi, H. Habazaki; Depth profiling analysis of passive films on molybdenum-containing stainless steel by glow discharge optical emission spectroscopy, AST2008, 2008.7.23-25, Rusutsu, Japan (2008).

K. Fushimi, S. Yamamoto, H. Habazaki; Micro-electrochemistry with flowing electrolyte-type scanning-droplet-cell, 59th Annual Meeting of the International Society of Electrochemistry, 2008.9.7-12, Seville, Spain (2008).

H. Habazaki, Y. Aoki, K. Fushimi, H. Mayama, T. Minami, Y. Oikawa, K. Tsujii; Formation and Wettability of Microcone-Type Porous Anodic Films on Niobium, 59th Annual Meeting of the International Society of Electrochemistry, 2008.9.7-12, Seville, Spain (2008).

K. Fushimi, K. Takakura, H. Habazaki, H. Konno, K. Azumi, S. Tsuri; Depassivation pH of Austenitic Stainless Steels in NaCl Aqueous Solution, Pacific Rim Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

T. Yamamoto, K. Fushimi, S. Miura, H. Habazaki, H. Konno; Effect of Hardness on Depassivation-repassivation Behavior of Pure Iron in Borate Buffer Solution Investigated by Micro-indentation, Pacific Rim Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

T. Fujii, Y. Aoki, K. Fushimi, T. Makino, S. Ono, H. Habazaki; Oblique Angle Deposition of Porous Al-Nb Alloys for Electrolytic Capacitor Application, Pacific Rim Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

Y. Oikawa, K. Fushimi, Y. Aoki, H. Habazaki, H. Konno; Growth of Porous Anodic Films on Niobium in Hot Phosphate-Glycerol Electrolyte, Pacific Rim

Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

M. Seo, N. Kikuchi, K. Fushimi, H. Habazaki, T. Nakayama; Anodic Behavior of Nickel in Acidic Perchlorate Solution Containing Pb^{2+}, Pacific Rim Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

M. Sakairi, T. Nakayama, S. Hashizume, K. Fushimi; Electrochemical Noise Analysis of 13 mass% Cr Stainless Steel HAZ by Solution Flow Type Micro-droplet Cell -Effect of Solution Concentration-, Pacific Rim Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

Y. Goto, M. Sakairi, T. Kikuchi, K. Fushimi; Fabrication of Micro-rods with a Solution Flow Type Electrochemical Droplet Cell, Pacific Rim Meeting on Electrochemical and Solid-state Science (PRiME 2008), 2008.10.12-17, Honolulu, USA (2008).

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Prof. H. Takahashi left LIMSA to Asahikawa National College of Technology as a president on March 2008, and Dr. H. Jha attended as postdoctoral researcher on April. After he left LIMSA, LIMSA was divided several research groups. Related members of our group are Asst. Prof. Dr. T. Kikuchi and students, S. Ueda, H. Shimaguchi, Y. Hara, Y. Wachi and S. Fujita.

Research work of our group directs toward 1) formation of novel of oxide film for dielectric materials, nano-materials, and anticorrosion film by anodizing and other thin film formation techniques, 2) development of new solution flow type micro-droplet cell and its application, and 3) establishment of localized corrosion mechanism of coated steels, titanium and aluminum alloys.

The topics of investigation are in the following:

(1) Corrosion of Al alloy in model tap water

Galvanic corrosion behavior of aluminum alloy in model tap waters was examined by electrochemical noise technique. In all model tap waters, after specimen was connected to Pt electrode, potential decrease with fluctuations and galvanic current increase with fluctuations. The current fluctuations and potential fluctuations show good correlation. After the experiments, there are corrosion products and micro pits were observed every samples surface. Therefore, each fluctuation could be related to each event, birth, propagation and death of pitting corrosion. The amplitude of both current and potential fluctuations was suppressed by addition of Ca^{2+}, Mg^{2+} and Cu^{2+}. The total amount of charge passed during the tests also decreases with addition of Ca^{2+}, Mg^{2+} and Cu^{2+}.

(2) Corrosion behavior of model cut edge face of coated steel

Focusing pulse YAG laser beam irradiation (PRM) was applied to form area ratio controlled model cut-edge on pre painted Zn and Zn-alloy coated steels. A corrosion behavior of formed model cut-edge was investigated by rest potential measurement in 1 mol m^{-3} NaCl with and without 0.5 kmol m^{-3} H_3BO_4/0.05 kmol m^{-3} $Na_2B_4O_7$. The rest potential showed almost constant value with fluctuations. The amplitude of fluctuations increased with exposed area of steel surface. White corrosion products of zinc oxide and simonkollite were formed after the experiments at the formed model cut-edge.

(3) Formation of 3D and layered structure by Sf-MDC

Solution flow type of micro droplet cell was applied to form high aspect ratio 3D microstructures on copper substrate. The use of an inner capillary tube as a mold during electrodeposition, makes it possible to form Cu micro-rods of about 15 mm length and about 100 μm diameter. The length is controlled by the deposition time. From X-ray analysis and surface observation, the formed Cu micro-rod is poly crystalline and the crystals are very fine. The cross section of the micro-rod was almost circular and the diameter did not change throughout its length. The conductivity of formed Cu micro-rods is about 11.8×10^6 S m^{-1}. This technique also makes it possible to form both straight metal structures as well as branched and layered micro-rods. This layered micro-rod fabrication technique can be applied to form resistance controlled micro wire.

(4) Anodic reaction of titanium in vitro by PRM

The repassibation kinetics of titanium was examined in Hanks by PRM (photon rupture method). In the experimental conditions, titanium was repassivated after oxide films were removed in Hanks by PRM. Every applied potential, the current after removed anodic oxide film in Hanks is larger than that in PBS. The slope after the current peak shows about -1.5. To add NaF in the Hanks, the current became larger even if applied potential was same. This result suggests that the initial dissolution rate was accelerated or repassivation reaction was inhibited by F^- ions.

(5) Corrosion behavior of aluminum alloy in shape controlled micro-pit

Corrosion type of aluminum and its alloys is usually pitting corrosion, therefore corrosion reaction in aspect ratio controlled micro pits is very important to understand influence of aspect ratio on corrosion. Combination of Photon rupture method (PRM) and anodizing techniques applied to form shape controlled micro-pit on aluminum alloy, and also examined the influence of aspect ratio on localized corrosion behavior of aluminum. Controlling laser irradiation time makes it possible to fabricate artificial micro-pits with different aspect ratio and to use aperture makes it possible to activate only bottom of micro-pit. Aspect ratio affects on repassivation kinetics in artificial pits.

(6) Formation of composite Al-Ti composite oxide film by LPD and anodizing

Liquid phase deposition is direct oxide film formation technique from solutions. This technique makes it possible to form oxide film or oxide particle without post heating. Electropolished aluminum specimens were coated with TiO_2 films by LPD, where the specimen covered with crystalline anodic oxide films was immersed in solutions containing Ti-fluoride and borate ions. After depositing TiO_2 films, the specimen was anodized to form Al-Ti composite oxide films. The composite oxide film on the specimens showed larger capacitances than aluminum anodic oxide films, and showed unique structure such as hemisphere shape. The size and number of the shape can be controlled by LPD condition.

(7) Electrochemical noise analysis of stainless steel in low pH NaCl solution.

Martensitic stainless steels are widely used oil field. The immersion corrosion test combined with microscopic technique is very important to examine susceptibility of SCC, SSC and HE. However, it is difficult to measure initiation time or progress of crack in-situ by immersion corrosion test. One of corrosion test to solve this problem is to use electrochemical technique such as electrochemical noise analysis (ENA). The ENA has been applied in a number of corrosion environments not only to investigate corrosion mechanism but also monitor initiation and propagation of localized corrosion and crack propagation. We applied ENA to investigate on initial stage of localized corrosion. The incubation period, average current density and amplitude of fluctuations change with potential. FFT method could be used to analyze current or potential fluctuations, that related pitting corrosion and crack propagation.

(8) Fabrication of low solution resistance solution flow type droplet cell

The droplet cell technique is a powerful widely applied tool to measure local electro chemical behavior and local surface treatment. We have developed a novel metal structure fabrication or patterning technique with a solution flow-type droplet cell with co-axis dual capillary tubes. However, this droplet cell has some problems, not 3 electrodes system, high solution resistance between counter electrode and working electrode. New type, 3 electrodes system, low solution resistance and high lateral resolution, was developed. To use this cell, it is possible to form micro-trench which width less than 80 μm. As applied suitable potential and scanning the cell on model composition change metal, it is also possible to measure current change by composition change.

(9) Formation of Al oxy-hydroxide nanofiber

Aluminum oxy-hydroxide nanofibers were formed from a porous anodic oxide film of aluminum. In the new method, the porous anodic aluminum oxide film not only acts as a template, but also serves as the starting material for the synthesis. The porous anodic oxide film is hydrothermally treated for pore-sealing, which forms aluminum oxy-hydroxide inside the pores of the oxide film as well as on the surface of the film. The hydrothermally sealed porous oxide film is immersed in the sodium citrate solution, which selectively etches the porous aluminum oxide from the film, leaving the oxy-hydroxide intact. The method gives highly uniform aluminum oxy-hydroxide nanofibers. The diameter of the nanofibers can be controlled by controlling the pore size of the porous anodic film. Nanofibers with diameters of about 38–85 nm, having uniform shape and size, were successfully synthesized using the present method.

Other activities

In July, Dr. H. Jha attended ASST2008 in Rusutsu, Japan and presented paper entitled "Metallization of Oxide/Hydroxide Film of Aluminum: The Palladium Activation Techniqes." He also got best poster presentation prize.

In September, Assoc. Prof. Sakairi attended Eurocorr 2008 in Edinburgh, United Kingdom and presented paper entitled " Corrosion Behavior of Al and Al Alloys in Dilute Chloride Ion Containing Solutions."

In October, Assoc Prof. Sakairi, Dr. Jha, and Mr. Goto attended the Prims, 214th Meeting of ECS - The Electrochemical Society. Assoc Prof. Sakairi presented papers entitled "Electrochemical noise analysis of 13 mass% Cr stainless steel HAZ by solution flow type micro-droplet cell- Effect of solution concentration-" and "Effect of aspect ratio of artificial pits formed on Al by PRM on localized corrosion in chloride environments". Dr. Jha presented paper entitled "Highly Uniform Aluminum Oxy-hydroxide Nanofiber from Porous Anodic Alumina". Mr. Goto presented paper entitled "Fabrication of micro-rods with a solution flow type electrochemical droplet cell".

Presentations

Electrochemical measurement on HAZ of stainless steel under stress, T. Nakayama, M. Sakairi, K. Fushimi and S. Hashizume, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, Jan., 2008.

Fabrication of model cut edge face on coated steel by Laser irradiation and its corrosion behavior, A. Kageyama and M. Sakairi, The Winter Joint Meeting of

The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, Jan., 2008.

Effect of cations on corrosion behavior of Al in fresh water, A. Kaneko, M. Sakairi, Y. Seki and D. Nagasawa, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, Jan., 2008.

Structure change of Al anodic oxide film by SPring-8 X-ray and electrochemical impedance, M. Sakairi, T. Suda, M. Sato, D. Nagasawa, Winter Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2008.

Structure change imaging by Electrochemistry and Analytical chemistry, M. Sakairi, ibid.

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Formation of Nb oxide film on Al by MO-CVD, N. Ishikawa, K. Nagahara, T. Kikuchi, M. Sakairi and H. Takahashi, ibid.

Formation of Ti-Al composite oxide film by LPD and anodizing, S. Koyama, T. Kikuchi, M. Sakairi and H. Takahashi, ibid.
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Formation novel composite oxide film for solid electoritic capacitor, N. Ishikawa, K. Nagahara, T. Kikuchi, M. Sakairi, H. Takahashi and K. Tamamitus, ibid.

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Effect of cold start on PEFC, M. Sakairi, H. Shirato, T. Suda, Y. Hamada, H. Hoshina, Y. Yamakosi, K. Tomita and Y. Oka, Zairyo-to-Kankyo 2008, Saitama, May, 2008.

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Structure controlled model cut edge face formation and its corrosion test, A. Kageyama, M. Sakairi and T. Kikuchi, ibid.

Fabrication of simple small electrochemical cell, M. Sakairi, Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Kiami, July, 2008.

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M. Sakairi, T. Kikuchi, Y Ohya and Y. Kojima, ibid.

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Fabrication of reusable printing roll by anodizing, Ni/Cu deposition and formation of conducting polymer, H. Shimaguchi, T. Kikuchi, M. Sakarii, H. Takahashi, K. Sato and R. Kubo, ibid.

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Repassivation kinetics of Ti in Hank's by PRM, M. Kinjyo, M. Sakairi and T. Kikuchi, The 55th Jpn. Conf. on Materials and Environments, Nagasaki, Sep., 2008.

Galvanic corrosion behavior of Al alloy in model tap water, A. Kaneko, M. Sakairi, T. Kikuchi, Y. Seki and D. Nagasawa, ibid.

Model edge face corrosion of Zn-alloy coating, A. Kageyama, M. Sakairi, T. Kikuchi, ibid.

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Highly Uniform Aluminum Oxy-hydroxide Nanofiber from Porous Anodic Alumina, H. Jha, T. Kikuchi, M. Sakairi and H. Takahashi, The fall meeting of J. Inst. Metal, Kumamoto, Sep., 2008.

Electrochemical noise analysis of 13 mass% Cr stainless steel HAZ by solution flow type micro-droplet cell- Effect of solution concentration-, M. Sakairi, T. Nakayama, T. Kikuchi, S. Hashizume and K. Fushimi, Prims,214th Meeting of ECS - The Electrochemical Society, Hawaii, Oct. 2008.

Effect of aspect ratio of artificial pits formed on Al by PRM on localized corrosion in chloride environments, M. Sakairi, A. Kageyama, Y. Kojima, Y. Oya and T. Kikuchi, ibid.

Fabrication of micro-rods with a solution flow type electrochemical droplet cell, Y. Goto, M. Sakairi, T. Kikuchi and K. Fushimi, ibid.

Fabrication of Three-Dimensional Actuators by Polypyrrole Micro-Patterning on Aluminum and Electrochemical Dissolution of Aluminum, T. Kikuchi, S. Ueda, M. Ueda, M. Sakairi and H. Takahashi, ibid.

Noise analysis of galvanic corrosion of Al alloy in model tap water, M. Sakairi, A. Kaneko, T. Kikuchi, Y. Seki and D. Nagasawa, The 115th fall meeting of light metal, Tokyo, Nov., 2008.

Corrosion behavior of anodized Al in high temperature alcohol, Y. Hara, T.

Kikuchi, M. Sakairi and H. Takahashi, ibid.

Facilities

AFM: SII SMP AFM with solution cell.
SEM: Hitachi TM-1000
Confocal scanning laser microscope Laser Tech. Co. 1SA-21
Pulse Laser system: 10Hz and 50 Hz pulsed Nd-YAG Laser with electric XYZ stage
Electrochemical AC Impedance: NF Circuit Design 5095 FRA equipped with potentiostat.

ABSTRACTS of PUBLICATIONS

Anodic dissolution of Ti in EMIC-$AlCl_3$ ionic liquid or LiCl-KCl molten salt for enhancement of adhesion between bone cell and Ti substrate

M. Ueda, T. Ohtsuka, K. Kuroda, R. Ichino, and M. Okido

Trans. Mater. Res. Soc. Jpn, 33, 779-782 (2008)

For application of Ti to the bio-implant materials, the anodic etching of Ti in the molten salt of LiCl-KCl and EMIC-$AlCl_3$ was investigated. The roughness of the Ti surface after the etching was examined from the SEM observation. The etching of the Ti electrode in the melt of LiCl-KCl did not form a suitably rough surface morphology. In the melt, the largely rough surface was formed with top-to-bottom distance of 10 µm. The etching in the melt of EMCI-$AlCl_3$ at the potential of 0.6 V vs. Al/Al(III) introduced the formation of a rough surface applicable to the Ti implant. The rough surface formed in the melt exhibits the top-to bottom distance of about 1 µm.

Electrodeposition of Sb-Te alloy in $AlCl_3$-NaCl-KCl molten salt

M. Ueda, Y. Mito, and T. Ohtsuka

Mater. Trans., 49, 1720-1722 (2008)

The Electrodeposition of Sb-Te alloy was carried out in $AlCl_3$-NaCl-KCl molten salt containing $SbCl_3$ and $TeCl_4$ at 423K by constant potential electrolysis. The voltammogram on a glassy carbon (GC) electrode in a melt containing 1.0×10^{-2} kmol m^{-3} [M] $SbCl_3$ and 1.0×10^{-2} M $TeCl_4$ revealed the cathodic current waves at 1.5, 1.1, and 0.9 V vs. Al/Al(III). A stable Sb-Te alloy deposit was obtained at 0.85 V in the melt containing $SbCl_3$ and $TeCl_4$. At the higher concentration ratio of the Sb(III) to (Sb(III) + Te(IV)), a good linear relation was found between the atomic ratio of Sb in the deposit and the concentration ratio of Sb (III) in the melt. The Sb-Te alloy deposit of atomic ratio of 38 : 62% which was assume to be suitable for a thermoelectric device was obtained with the molten salt containing 7.0×10^{-3} M $SbCl_3$ and 1.0×10^{-2} M $TeCl_4$. The XRD pattern of the deposit corresponds to that of Sb_2Te_3 intermetallic compound. The deposit had homogeneous disk-like granule with the disk size of about 10 μm.

Electrochemical behavior and alloy deposition of Bi, Sb, and Te in chloride molten salt

M. Ueda, H. Ebe, S. Tsuchiya and T. Ohtsuka

Molten Salts, 51, 194-200 (2008)

The Electrochemistry of Sb, Bi, and Te in $AlCl_3$–NaCl–KCl molten salt containing $SbCl_3$, $BiCl_3$, and/or $TeCl_4$ at 423K was investigated by voltammetry, and alloy electrodeposition of the three metals was performed under constant potential control and potential pulse control in the melt. The voltammogram on a glassy carbon (GC) electrode in a melt containing 0.025 mol dm^{-3} [M] $SbCl_3$ showed a couple of redox peak corresponding to the Sb/Sb(III) redox reaction, and a stable layer of pure Sb was deposited under the constant potential control. The voltammograms in the melt containing 0.025M $BiCl_3$ or 0.025M $TeCl_4$ showed several redox couples. A stable Bi–Te alloy deposit was obtained with the molten salt containing $BiCl_3$ and $TeCl_4$. The Bi–Sb-Te alloys were also deposited in the melt containing $SbCl_3$, $BiCl_3$, and $TeCl_4$ by using constant potential electrolysis and potential pulse electrolysis. From the electrodeposition results it is seen that the $SbCl_3$ concentration is effective to control the composition of Bi-Sb-Te ternary alloy. The electrodeposit $Bi_{0.5}Sb_{1.5}Te_3$ which is thought to be one of best thermoelectric conversion device was obtained on glassy carbon. The alloy deposits had good crystallinity and the preferential orientation was the (1 1 0) plane. (in Japanese)

The effect of ultrasonic irradiation during electropolymerization of polypyrrole on corrosion prevention of the coated steel

Damian Kowalski, Mikito Ueda and Toshiaki Ohtsuka

Corrosion Science, 50 (2008) 286-291

Ultrasonic irradiation was imposed during electropolymerization of polypyrrole (PPy) in acid phosphate solution containing molybdophosphate ions and pyrrole monomer. Corrosion of the steel coated by the PPy film prepared under ultrasonic irradiation was tested in 3.5 wt.% NaCl solution and compared with corrosion of the steel coated by the PPy film without ultrasonic irradiation. The PPy film prepared under ultrasonic irradiation kept the steel in the passive state one and a half times as long as that prepared without ultrasonic irradiation. Imposition of ultrasound enhanced the doping of $PMo_{12}O_{40}^{3-}$ and decreased the doping of HPO_4^{2-}. The surface morphology of the PPy film was changed with imposition of ultrasound in electropolymerization process. Under imposition of ultrasound, a dense and compact PPy layer was formed. The structure of the PPy film obtained under ultrasonic irradiation was assumed to result from change in nucleation-growth mechanism.

Phospholipid-linked quinones-mediated electron transfer on an electrode modified with lipid bilayers

Yoshiharu Suemori, Morio Nagata, Masaharu Kondo, Syuichi Ishigure, Takehisa Dewa, Toshiaki Ohtsuka and Mamoru Nango

Colloids and Surfaces B: Biointerfaces, 61 (2008) 286-291.

Phospholipid-linked naphthoquinones separated by spacer methylene groups (C*n*), PE-C*n*-NQ ($n = 0$, 5, 11), were synthesized to investigate the quinone-mediated electron transfers on a glassy carbon (GC) electrode covered with phospholipids membrane. The PE-C*n*-NQ could be incorporated in lipid bilayer composed of phosphatidylcholine and exhibited characteristic absorption spectral change corresponding to their redox state, quinone/hydroquinone. The cyclic voltammogram of PE-C*n*-NQ-containing lipid bilayer modified on a GC electrode indicated a set of waves corresponding to the consecutive two-electron and two-proton transfer reduction of the quinone moiety. The peak currents of PE-C*n*-NQ as a function of temperature showed a sharp break point in the current–temperature behavior, reflecting the gel-fluid phase transition. The shape of the cyclic voltammograms changed with the pH of the buffer solution. Below pH 6 the first step of the reduction of quinone was a monoprotonation of quinone, whereas above pH 10 the first step of the oxidation was a monodeprotonation of hydroquinone. This indicates that reaction sequences of quinone/hydroquinone were different with the change of the pH. These results showed that the PE-C*n*-NQ exhibited electron transfer associated with proton transfer in the lipid membranes, depending on the diffusivity of the redox species in the membrane and pH. Interestingly, less effect of the number of methylene of the spacer group on the peak currents was observed. Comparison of manganese porphyrin-mediated electron transfer depends on the spacer methylene lengths.

Electron transfer of quinone self-assembled monolayers on a gold electrode

Morio Nagata, Masaharu Kondo, Yoshiharu Suemori, Tsuyoshi Ochiai, Takehisa Dewa, Toshiaki Ohtsuka and Mamoru Nango

Colloids and Surfaces B: Biointerfaces, 64 (2008) 16-21.

Dialkyl disulfide-linked naphthoquinone, $(\text{NQ-C}n\text{-S})_2$, and anthraquinone, $(\text{AQ-C}n\text{-S})_2$, derivatives with different spacer alkyl chains (C*n*: $n = 2, 6, 12$) were synthesized and these quinone derivatives were self-assembled on a gold electrode. The formation of self-assembled monolayers (SAMs) of these derivatives on a gold electrode was confirmed by infrared reflection-absorption spectroscopy (IR-RAS). Electron transfer between the derivatives and the gold electrode was studied by cyclic voltammetry. On the cyclic voltammogram a reversible redox reaction between quinone (Q) and hydroquinone (QH_2) was clearly observed under an aqueous condition. The formal potentials for NQ and AQ derivatives were −0.48 and −0.58 V, respectively, that did not depend on the spacer length. The oxidation and reduction peak currents were strongly dependent on the spacer alkyl chain length. The redox behavior of quinone derivatives depended on the pH condition of the buffer solution. The pH dependence was in agreement with a theoretical value of $E_{1/2}$ (mV) $= E' - 59\text{pH}$ for $2H^+/2e^-$ process in the pH range 3–11. In the range higher than pH 11, the value was estimated with $E_{1/2}$ (mV) $= E' - 30\text{pH}$, which may correspond to $H^+/2e^-$ process. The tunneling barrier coefficients (β) for NQ and AQ SAMs were determined to be 0.12 and 0.73 per methylene group (CH_2), respectively. Comparison of the structures and the alkyl chain length of quinones derivatives on these electron transfers on the electrode are made.

Surface oxide film and its influence on the oxygen reduction on Pd-Co and Pt-Co FEFC cathodes

Y. Tamura, K. Taneda, M. Ueda, and T. Ohtsuka

ECS Transaction, 16 (2) (2008) 741-750.

Pt-Co and Pd-Co alloy electrodes were investigated in a 0.5 M sulfuric acid solution by electrochemistry, ellipsometry, laser Raman scattering spectroscopy, XPS, and GD-OES. The corrosion resistivity of Pt-Co and Pd-Co alloys decreased with increase of Co addition. The influence of Co addition, however, enhanced the catalytic efficiency on the ORR. The alloy surfaces may be covered by CoOOH and Pt or Pd oxide 2-3 nm thick. At the potential of 1.2 V vs. Ag/ AgCl/ sat. KCl, the thickness of oxide film increased with the Co addition. The presence of the oxide film on the alloy electrodes increases the over voltage for the ORR. The effect of the oxide thickness on the ORR was discussed.

Oblique Angle Deposition of Columnar Niobium Films for Capacitor Application

M. T. Tanvir, K. Fushimi, Y. Aoki and H. Habazaki

Materials Transactions, **49**, 1320-1326 (2008)

Niobium films with isolated columnar morphology have been prepared by oblique angle magnetron sputtering for capacitor application. Anodizing of the deposited mobium to form dielectric mobium oxide reduces the surface roughness, since the gaps between the neighboring columns are filled with the oxide due to large Pilling-Bedworth ratio for Nb/Nb_2O_5. To increase the gaps between neighboring columns, the influences of the angle of mobium flux to substrate and substrate surface roughness on the columnar morphology of the deposited films have been investigated using scanning electron microscopy and the electrochemical measurements. The deposition on the textured rough substrate surface and at higher angle of the mobium flux from normal to the substrate surface fabricates the mobium films with higher surface roughness.

Barrier and Porous Anodic Oxides on InSb

A. Suleiman, T. Hashimoto, P. Skeldon, G. E. Thompson, F. Echeverria, M. J. Graham, G. I. Sproule, S. Moisa, H. Habazaki, P. Bailey and T. C. Q. Noakes

Corrosion Science, **50**, 1353-1359 (2008)

Anodizing of InSb at 5 mA cm^{-2} in sodium tungstate electrolyte is shown to produce barrier-type amorphous oxide at relatively low voltages, to about 40 V, and porous-type amorphous oxide at increased voltages. The barrier-type amorphous oxide, consisting of units of In_2O_3 and Sb_2O_3, distributed relatively uniformly throughout the film, develops at a formation ratio of 2.2 ± 0.2 nm V^{-1}. The outer 15-20% of the film also contains tungsten species. The relatively high efficiency of barrier film growth reduces significantly with transition to porous oxide, which is associated additionally with generation of oxygen at the film surface. The final oxide, at 65 V, comprises pores, of typical diameter 80 nm, orientated approximately normal to the substrate and extending from a barrier region to the film surface.

Effect of Underpotential Deposition of Lead on Polarization Behavior of Nickel in Acidic Perchlorate Solutions at Room Temperature

M. Seo, K. Fushimi, H. Habazaki and T. Nakayama

Corrosion Science, **50**, 3139-3146 (2008)

The effect of Pb^{2+} on polarization behavior of nickel has been investigated in 0.1 M $NaClO_4$ + 10^{-2} M $HClO_4$ + x M PbO solutions (x=0, 10^{-5}, 10^{-4}, 10^{-3}) at room temperature. The cyclic voltammogram has suggested that Pb^{2+} degrades the stability of the passive film on Ni. The corrosion potential of Ni shifted to the more noble direction and the anodic current peak of Ni dissolution decreased with increasing Pb^{2+} concentration in solution, indicating that Pb^{2+} suppresses significantly the anodic dissolution. The underpotential deposition (UPD) of lead on Ni in the potential range more noble than -0.215 V (SHE) corresponding to the equilibrium potential of the Pb^{2+} (10^{-3} M)/Pb electrode was confirmed by XPS and GDOES analyses. The anodic Tafel slope, b^+, of Ni dissolution changed from b^+=40 mV decade^{-1} in the absence of Pb^{2+} to b^+=17 mV decade^{-1} in the presence of 10^{-4} or 10^{-3} M Pb^{2+}, which was ascribed to the increase in active sites of Ni surface emerged as a result of electrodesorption of Pb adatoms. The roles of Pb adatoms in active dissolution and active/passive transition of Ni were discussed from the above results.

Photocurrent Spectroscopy Applied to the Characterization of Passive Films on Sputter-deposited Ti-Zr Alloys

M. Santamaria, F. Di Quarto and H. Habazaki

Corrosion Science, **50**, 2012-2020 (2008)

A photoelectrochemical investigation on thin (≤ 13 nm) mixed oxides grown on sputter-deposited Ti-Zr alloys of different composition by air exposure and by anodizing (formation voltage, U_F=4 V/SCE) was carried out. The experimental results showed that the optical band gap increases with increasing Zr content in both air formed and anodic films. Such behaviour is in agreement with the theoretical expectation based on the correlation between the band gap values of oxides and the difference of electronegativity of their constituents. The flat band potential of the mixed oxides was found to be almost independent on the Ti/Zr ratio into the film and more anodic with respect to those estimated for oxide grown on pure Zr. The semiconducting or insulating character of the investigated films was strongly influenced by the forming conditions and the alloy composition.

Influences of Structure and Composition on the Photoelectrochemical Behaviour of Anodic Films on Zr and Zr-20 at.%Ti

M. Santamaria, F. Di Quarto and H. Habazaki

Electrochimica Acta, **53**, 2272-2280 (2008)

A photoelectrochemical investigation on anodic films of different thickness grown on sputter-deposited Zr and Zr-20 at.%Ti was carried out. The estimated optical band gap and flat band potential of thick ($U_F \leq 50$ V) anodic films were related to their crystalline structure and compared with those obtained for thinner ($U_F \leq 8$ V/SCE) anodic oxides having undetermined crystalline structure. The Eg values obtained by photocurrent spectroscopy were also compared with the experimental band gap estimated by other optical ex situ techniques and with the available theoretical estimates of the zirconia electronic structures in an attempt to reconcile the wide range of band gap data reported in the literature. Finally, the optical band gap and flat band potential values obtained for tetragonal $Zr_{0.8}Ti_{0.2}O_2$ mixed oxide were compared with that expected on the basis of a correlation between E_g and the film composition.

Growth of Porous Anodic Films on Niobium in Hot Phosphate-glycerol Electrolyte

Y. Oikawa, K. Fushimi, Y. Aoki and H. Habazaki

ECS Transactions, **16**, 345-351 (2008)

Porous anodic films have been developed on niobium at constant formation voltages between 5 and 50 V in glycerol electrolyte containing 0.8 mol dm-3 dibasic potassium phosphate at 433 K. Except at the formation voltage of 5 V, at which the current density is approximately constant during anodizing, the current shows the minimum and then maximum. After the current maximum, the current density decreases gradually, which follows the Cottrell equation. Thus, diffusion of some species in the pores should control the growth rate of the anodic films. The porous films developed are practically Nb_2O_5 with a small amount of carbon contamination. Incorporation of phosphorus species, which often occurs in aqueous electrolytes, is negligible at all the formation voltages in the present electrolyte. Based on the results obtained, the growth process of the porous anodic films on niobium in this hot organic electrolyte is discussed.

Influence of Grain Orientation on Oxygen Generation in Anodic Titania

E. Matykina, R. Arrabal, P. Skeldon, G. E. Thompson and H. Habazaki

Thin Solid Films, **516**, 2296-2305 (2008)

The influence of grain orientation on oxygen generation during anodizing of chemically polished titanium at 20 mA cm^{-2} in 0.026 M Na_3PO_4 and 0.02 M $Na_4P_2O_7$ is investigated in the pre-sparking region using scanning electron, atomic force and transmission electron microscopies. The findings reveal preferential oxygen generation in the anodic film on titanium grains that tend to a basal-like orientation. The resultant oxygen-filled voids that develop within the film increase in size and coalesce with progress of anodizing. Their presence leads to formation of blisters and the eventual film rupture due to release of the high-pressure gas. In contrast, relatively few voids, and hence smoother film, develop on grains of prism-like orientation. The differing rates of oxygen generation are attributed to the grain orientation dependence of the amorphous-to-crystalline transition of anodic titania, with rutile being identified at sites of oxygen-filled voids in films formed in 0.02 M $Na_4P_2O_7$. There may also be small contributions to oxygen generation from influences of substrate impurities incorporated into the film. The grain orientation also affected the rate of chemical polishing of the titanium in HF/HNO_3, which was faster on basal-like planes.

Porous Anodic Oxides on Titanium and on a Ti-W Alloy

Q. Lu, J. Alberch, T. Hashimoto, S. J. Garcia-Vergara, H. Habazaki, P. Skeldon and G. E. Thompson

Corrosion Science, **50**, 548-553 (2008)

The growth of a nanoporous anodic oxide oil titanium and a Ti-20 at.% W alloy, both deposited by magnetron sputtering, ill a glycerol/phosphate electrolyte at 453 K is reported. The oxide formed on titanium is a mixture of amorphous titania and anatase. However, that on the alloy is amorphous only and forms at increased efficiency, about 27%. The amorphous structure is considered to be stabilized by incorporated units of WO_3, which are distributed uniformly throughout the anodic film. The growth of the porous oxides is suggested to be associated with loss of film species at the film/electrolyte interface at the base of pores, with new oxide forming exclusively at the metal/film interface by inward migration of O^{2-} ions.

Behaviour of Copper during Alkaline Corrosion of Al-Cu Alloys

Y. Liu, M. A. Arenas, S. J. Garcia-Vergara, T. Hashimoto, P. Skeldon, G. E. Thompson, H. Habazaki, P. Bailey and T. C. Q. Noakes

Corrosion Science, **50**, 1475-1480 (2008)

Enrichment of copper beneath amorphous anodic films on relatively dilute, solid-solution Al-Cu alloys is necessary before copper can be oxidized and incorporated into the oxide layer. A similar enrichment arises during electropolishing, which also develops an amorphous oxide. In these cases, external polarization is applied, usually generating a relatively high oxidation rate. In contrast, enrichment behaviour at the corrosion potential has received less attention. The present study examines the corrosion of Al-Cu alloys, containing up to 6.7 at.% Cu, in 0.1 M sodium hydroxide solution at 293 K. Copper is again found to enrich in the alloy, similarly to behaviour with anodic polarization. However, following enrichment, discrete copper-rich particles appear to be generated in the corrosion product. These are suggested to be nanoparticles of copper, since the corrosion potentials of the alloys are low relative to that required for oxidation of copper. The corrosion rate increases with increase of both time and copper content of the alloy, probably associated with a greater cathodic activity due to an increasing number of nanoparticles. The corrosion proceeds with loss of aluminium species to the sodium hydroxide solution, but with retention of copper in the layer of hydrated alumina corrosion product.

Tracer Investigation of Pore Formation in Anodic Titania

D. J. LeClere, A. Velota, P. Skeldon, G. E. Thompson, S. Berger, J. Kunze, P. Schmuki, H. Habazaki and S. Nagata

Journal of the Electrochemical Society, **155**, C487-C494 (2008)

Using a sputtering-deposited titanium substrate, incorporating six equally spaced nanolayers of Ti-W alloy, the volume and composition changes accompanying the formation of porous anodic films on titanium in 0.5 wt % NH_4F in glycerol are investigated. The findings reveal amorphous films with nanotubes of TiO_2, containing fluoride ions and possibly glycerol derivatives. Tungsten and titanium species are lost to the electrolyte at differing rates during anodizing, leading to an enrichment of tungsten in the film relative to the composition of the substrate. The spacing of tungsten-containing bands in the film is similar to 2.3 that of the original alloy layers during growth of the major pores. The generation of the nanotubes can be explained either by field-assisted flow of film material within the barrier layer to the pore walls, with cation and anion transport numbers of anodic titania in the barrier layer region similar to those of barrier films and with field-assisted ejection of Ti^{4+} ions to the electrolyte, or by field-assisted dissolution, but with a reduction in cation transport number.

Electrochemical Capacitance of Nitrogen-containing Nanocarbons Prepared Using Porous Anodic Alumina Template

M. Kiriu, K. Fushimi, H. Konno and H. Habazaki

Electrochemistry, **76**, 197-202 (2008)

Nanocarbons with brush-type morphology have been prepared by liquid phase carbonization of poly(acrylamide) (PAA) or poly(vinylchloride) (PVC) in pores of template. The template used is dc etched aluminum foil that is further anodized in sulfuric acid electrolyte. The nanocarbons derived from PAA contain nitrogen, whose content decreases with increasing heat treatment temperature. At each heat treatment temperature, the specific surface area as well as pore structure is similar for both the nanocarbons derived from PAA and PVC. Nevertheless, the markedly large electrochemical capacitance, measured in 1 mol dm^{-3} sulfuric acid, is obtained for the PAA-derived nanocarbons, compared with that from PVC, due to pseudocapacitance arising from nitrogen species in the former nanocarbons. Despite the specific surface area of less than 250 m^2 g^{-1}, the PAA-derived nanocarbons reveal the capacitance as large as ~130 F g^{-1}. The capacitance per specific surface area is found to increase almost linearly with the content of nitrogen. It is also found that the capacitance per specific surface area of the nanocarbons with the brush-type morphology is larger than that of the carbon nanofilaments prepared similarly using a template of porous anodic alumina on plain aluminum foil.

Thermal Degradation of Anodic Niobia on Niobium and Oxygen-containing Niobium

H. Habazaki, M. Yamasaki, T. Ogasawara, K. Fushimi, H. Konno, K. Shimizu, T. Izumi, R. Matsuoka, P. Skeldon and G. E. Thompson

Thin Solid Films, **516**, 991-998 (2008)

Thermal treatment of anodized niobium and oxygen-containing niobium has been carried out to elucidate the thermal degradation mechanism of niobium capacitors and to clarify the influence of oxygen dissolved in niobium on thermal degradation. The capacitance and leakage current of the anodized specimens increase with thermal treatment above 423 K in air, although the oxygen content in the substrate has no significant effect up to 523 K. At increased temperatures, the changes in capacitance and leakage current are suppressed with increasing oxygen content. The anodic film formed on the Nb-50 at.% O substrate thickens significantly during thermal treatment at 623 K in air, while only a slight reduction of the thickness is evident for those on the niobium and Nb-20 at.% O substrates. In contrast, vacuum thermal treatment at 623 K causes thinning of the anodic film on niobium, with evidently no change in the film thickness on the Nb-50 at.% O substrate. These are interpreted in terms of oxygen diffusion from the anodic film to the substrate as well as thermal oxide growth.

Inhibition of Field Crystallization of Anodic Niobium Oxide by Incorporation of Silicon Species

H. Habazaki, T. Ogasawara, K. Fushimi, K. Shimizu, S. Nagata, T. Izumi, P. Skeldon and G. E. Thompson

Electrochimica Acta, **53**, 8203-8210 (2008)

The present work demonstrates effective inhibition of field crystallization of amorphous anodic niobium oxide by incorporation of silicon species from substrate. The field crystallization, detrimental for capacitor application of niobium, occurs during anodizing of magnetron sputtered niobium at 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K, while amorphous structure of the anodic oxide is totally retained during anodizing of magnetron sputtered Nb-12 at% Si. Even after prior thermal treatment in air, which accelerates field crystallization of anodic oxide on niobium, no crystallization occurs on the Nb-12 at% Si. Through examination of the crystallization behaviours of anodic films formed on a thin Nb-12 at% Si layer superimposed on a niobium layer as well as on a thin niobium layer superimposed on an Nb-12 at% Si layer, it has been confirmed that air-formed oxide or thermal oxide becomes a nucleation site for crystallization. Modification of the air-formed or thermal oxide by incorporation of silicon species inhibits the nucleation of crystalline oxide. The modification, however, does not influence the growth of crystalline oxide. The growth is suppressed by continuous incorporation of silicon species into anodic film from the substrate during anodizing.

Behaviour of a Fast Migrating Cation Species in Porous Anodic Alumina

S. J. Garcia-Vergara, P. Skeldon, G. E. Thompson and H. Habazaki

Corrosion Science, **50**, 3179-3184 (2008)

The behaviour of Nd^{3+} ions is examined in porous anodic alumina films formed at 5 mA cm^{-2} in 0.4 M phosphoric acid at 293 K on aluminium substrates that contain a buried 5 nm-thick tracer band of Al-Nd alloy. The Nd^{3+} ions migrate outward in the barrier region about twice as fast as Al^{3+} ions. The neodymium was located in the anodic film by transmission electron microscopy and scanning electron microscopy, and quantified by Rutherford backscattering spectroscopy. The Nd^{3+} ions migrated to the cell walls and to pore base, depending upon their location in the substrate relative to the alumina cells and pores. Nd^{3+} ions that reached the pore base were lost to the electrolyte. The outward transport of the Nd^{3+} ions was greatest beneath the pores and least at the cell boundaries, resulting in transformation of the planar tracer layer of the substrate to a roughly hemispherical shape in the film. The behaviour contrasts with that of a tracer band of slowly migrating W^{6+} ions, which reveals an approximately inverse distribution, while W^{6+} ions are retained within the film.

Incorporation of Gold into Porous Anodic Alumina Formed on an Al-Au Alloy

S. J. Garcia-Vergara, M. Curioni, F. Roeth, T. Hashimoto, P. Skeldon, G. E. Thompson and H. Habazaki

Journal of the Electrochemical Society, **155**, C333-C339 (2008)

An Al-1 atom % Au gold alloy is employed to investigate the incorporation of a nonoxidized alloying element into porous anodic alumina films formed in phosphoric acid and sulfuric acid electrolytes. Gold is shown to enrich in the alloy in the initial stages of film growth, when a gold-free film is formed. On sufficient enrichment of the alloy, gold nanoparticles are incorporated into the film above an enriched alloy layer containing nanocrystals of Al_2Au. The formation of the nanoparticles is accompanied by a reduced rate of film growth due to generation of oxygen. The gold is incorporated into the films preferentially at the cell boundary regions of the scalloped alloy/film interface. Elongated and approximately circular nanoparticles are observed in film sections, the former type being particular to films formed in sulfuric acid electrolyte. The incorporation of gold into the film commences earlier than predicted for a planar alloy/film interface. The behavior suggests that transport of gold occurs within the enriched alloy layer, possibly associated with the stresses at the alloy/film interface due to film growth processes.

Thickness Dependence of Proton Conductivity of Amorphous Aluminosilicate Nanofilm

Y. Aoki, H. Habazaki and T. Kunitake

Electrochemical and Solid State Letters, **11**, P13-P16 (2008)

$Al_xSi_{1-x}O_n$ films exhibit a drastic change of proton conductivity across the film by reducing their thickness to less than 100 nm. The temperature and humidity dependence of conductivity of the sub-100 nm films is quite different from those of the thicker films. Furthermore, in the former thickness range, the value of conductivity markedly increases with reducing the film thickness, and its thickness dependence follows a power law with a fixed index of -2.1. This size-scaling effect can be explained by the percolation conductivity model that the probability for percolating of the conductive moiety in $Al_xSi_{1-x}O_n$ films increases with decreasing the thickness.

Changes in Surface Stress of Au Electrode during Underpotential Deposition of Bi and Pb

Masahiro Seo and Makiko Yamazaki

ECS Transactions, **11**, 13-21 (2008)

The changes in surface stress of Au electrode (mainly oriented to (111) plane) during underpotential deposition (UPD) of Bi and Pb were measured by a bending beam method to investigate the relation between surface stress and structure of the adlayer. The surface stress changed to the compressive direction as Bi- or Pb-UPD proceeded. The changes in surface stress to the compressive direction responded sensitively to the structural changes of the Bi- or Pb-adlayer. The biaxial modulus of (p x $\sqrt{3}$)-2Bi monolayer or hexagonal close-packed Pb monolayer on Au (111) electrode was estimated from the relation between the changes in surface stress and the surface elastic strain of the monolayer obtained by surface X-ray scattering. The factors influencing the changes in surface stress during UPD of Bi or Pb were discussed in connection with the structural changes of the adlayer.

Interfacial Reactions in Nb/NbSi$_2$ and Nb/NbSi$_2$-B systems

M. Ukegawa, A. Yamauchi, A. Kobayashi and K. Kurokawa

Vacuum, 83, 157-160 (2008)

For the use of Nb-based alloys at high temperatures, a high oxidation resistant coating such as NbSi$_2$ coating is required. In the present study, to clarify the physico-chemical compatibility between Nb and NbSi$_2$, the extent of the interfacial reaction and the reaction products were studied at temperatures ranging from 1573 to 1773 K. Growth of the reaction layer formed by the interfacial reactions was caused by the preferential diffusion of Si toward the Nb side, leading to the formation of a Nb$_5$Si$_3$ layer. The growth followed a parabolic rate law, and the growth rate constant was expressed as kp (m^2 s^{-1}) 7.98× 10^{-10} exp (-131.84 kJ mol^{-1}/RT). In addition, behavior of boron in the Nb/NbSi$_2$ interfacial reaction was clarified.

Experimental Determination of Isothermal Phase Diagram at 1423 K in the Ternary Re-Cr-Ni System

S. Saito, K. Kurokawa, S. Hayashi, T. Takashima and T. Narita

J. Japan Inst. Metals, 72, 132-137 (2008)

Compositions with tie-lines between the γ, α, σ, and δ phases in a ternary Re-Cr-Ni system were investigated by heat-treating various ternary Re-Cr-Ni alloys in vacuum at 1423 K for a variety of heating times up to 2500 h. The microstructures of the Re-Cr-Ni alloys that had been water-quenched after heating were observed and their Re, Cr and Ni concentration profiles were measured using an electron probe micro-analyzer (EPMA). It was found that a very long heat treatment was required to obtain equilibrium compositions of Ar-arc-melted Re-Cr-Ni alloys.

The tie-line compositions (at%) of each phase at 1423 K were experimentally determined, and an isothermal phase diagram was constructed. From these results, the γ, α, and σ phases of the three-phase coexistence state were found to have the following compositions: γ phase (3.0 at%Re, 45.6 at%Cr, and 51.4 at%Ni), α phase (16.1 at%Re, 75.2 at%Cr, and 8.7 at%Ni), and σ phase (16.3 at%Re, 60.3 at%Cr, and 23.4 at%Ni). In addition, the γ, σ, and δ phases have the following compositions: γ phase (13.3 at%Re, 18.1 at%Cr, and 68.6 at%Ni), σ phase (54.6 at%Re, 24.2 at%Cr, and 21.2 at%Ni), and δ phase (70.2 at%Re, 6.0 at%Cr, and 23.8 at%Ni).

The solubility limits of Ni in the σ phase increased from 19 at%Ni to 24 at%Ni, as the Cr content in the σ phase with a tie-line with the γ phase increased from 23 at%Cr to 61 at%Cr. (in Japanese)

Tie-Lined Compositions of the σ and (γ, γ ', β) Phases in a Ni-Al-Re-Cr System at 1423 K

S. Saito, K. Kurokawa, T. Takashima and T. Narita

J. Japan Inst. Metals, 72, 639-643 (2008)

Compositions with tie-lines between the σ and (γ, γ ', β) phases in a quaternary Ni-Al-Re-Cr system were investigated by heat-treating various quaternary Ni-Al-Re-Cr alloys in vacuum at 1423 K for a variety of heating times up to 2750 h. The microstructures of the Ni-Al-Re-Cr alloys that had been water-quenched after heating were observed and their Ni, Al, Re, and Cr concentration profiles were measured using an electron probe micro-analyzer (EPMA). It was found that a very long heat treatment was required to obtain equilibrium compositions of Ar-arc-melted Ni-Al-Re-Cr alloys.

The tie-lined compositions (at%) of each phase at 1423 K were experimentally determined as follows. The σ phase tie-lined with the γ phase (73.5Ni, 14.6Al, 2.9Re, and 9.0Cr) consists of 56.7Re, 25.0Cr, 18.1Ni, and 0.2Al. The σ phase tie-lined with the γ phase (70.5Ni, 14.3Al, 2.0Re, and 13.2Cr) has 47.7Re, 36.2Cr, 15.9Ni, and 0.2Al. The σ phase tie-lined with the γ ' phase (73.6Ni, 21.0Al, 1.2Re, and 4.2Cr) consists of 58.3Re, 25.0Cr, 16.6Ni, and 0.1Al. The σ phase tie-lined with the β phase (50.2Ni, 48.7Al, 0.3Re, and 0.8Cr) consists of 61.1Re, 32.5Cr, 5.2Ni, and 1.2Al. The σ phase tie-lined with the β phase (65.1Ni, 29.5Al, 0.4Re, and 5.0Cr) consists of 45.8Re, 39.3Cr, 14.6Ni, and 0.3Al. (Japanese)

Microanalysis of Oxide Scales Formed on Sintered Cr-Si-Ni.

Y. Suzuki, A. Yamauchi, A. Kobayashi and K. Kurokawa

Frontier of Applied Plasma Technology, 1, 65-68 (2008)

Materials which from a SiO_2/Cr_2O_3 double-layer scale are expected to have excellent high-temperature corrosion resistance. For formation of the double-layer scale, the Cr-Si-Ni alloys were proposed in the present study. The sintered alloys mainly consisted of $CrSi_2$ and (Cr, Ni)Si phases. The oxide scales formed on the Cr-Si-Ni alloys with various Ni contents at 1273 K were observed and analyzed by TEM and TEM-EDS. It was found that $CrSi_2$-(5, 10, 20, 40) mass%Ni alloys formed the SiO_2/Cr_2O_3 scale. However, the relative thickness of SiO_2 layer to Cr_2O_3 layer in the oxide scale depended on the concentration ratio of $CrSi_2$ in the substrate. The optimum composition was estimated to be (Cr-66.6mole%Si) -10mass%Ni. The alloy showed an outstanding high-temperature corrosion resistance.

High-Temperature Oxidation Behavior of B Added WSi_2 in H_2O-Containing Atmospheres.

K. Tanaka, A. Yamauchi and K. Kurokawa

Journal of Applied Plasma Science, 16, 64-68 (2008)

Oxidation tests of B added WSi_2 fabricated by a spark plasma sintering methods were carried out in H_2O-containing atmospheres at temperatures ranging from 773 to 1473 K. The B added WSi_2 showed excellent oxidation resistance due to the formation of a protective borosilicate scale in H_2O-containing atmospheres. The thicknesses of dense borosilicate scales formed at 1273 K and above were about 1-2 μm. On the other hand, the morphology of borosilicate scale formed at 1073 K for up to 180 ks consisted of a thin SiO_2 and hemispherical borosilicate scales. Such morphology might be due to the reaction of borosilicate with water vapor, and the difference between evaporation rate of borosilicate and the rate of B diffusion from the substrate to scale. (in Japanese)

Microstructure and Oxidation Behavior of Boron-Added WSi_2 Compact.

A. Yamauchi, T. Sasaki, A. Kobayashi and K. Kurokawa

Materials Transactions, 49, 2047-2053 (2008)

In order to improve the oxidation resistance of WSi_2 at 873–1473K, B added WSi_2 was fabricated by a spark plasma sintering method and oxidation tests were carried out in air. The fabricated B added WSi_2 consists of WSi_2, Si and W_2B_5. The addition of B into WSi_2 leads to the formation of a protective borosilicate scale, resulting in improvement of the oxidation resistance. Requisite concentration of B for the formation of a protective borosilicate scale decreases as the temperature is raised. Consequently, the addition of 2 or 3 mass% B is the most effective for improvement of the oxidation resistance of WSi_2 in the temperature range of 873–1473K. Such effect of B on high-temperature oxidation of WSi_2 is also discussed.

Numerical Simulation of Solidified Structure Formation of Al-Si Alloy Casting Using Cellular Automation Method.

K. Ohsasa, K. Matsuura, K. Kurokawa, and S. Watanabe

Materials Sci. Forum, 575-578, 154-163 (2008)

For the purpose of the prediction of casting structures, heterogeneous nucleation rate in the undercooled melt of solififying Al-Si alloys were evaluated by comparing experimentally observed macrostructures of solidified ingots with numerically simulated ones. Molten alloys were unidirectionally solidified in an adiabatic mold from a steel chill block located at the bottom of the mold. In the experiment, columnar to equiaxed transition (CET) was observed. A numerical simulation for grain structure formation of the sample ingots was carried out using a cellular automaton (CA) method, and heterogeneous nucleation rate in the solidifying alloys were evaluated by producing the similar structures to experimental ones. An attempt was made to predict the grain structure of conventionally cast ingots using the evaluated heterogeneous nucleation rate. However, the simulation could not predict the structure of ingot with low superheat due to crystal multiplication near the mold wall. The crystal multiplication mechanism, so-called "Big Bang mechanism", was introduced into the simulation and the simulation could predict the grain macrostructure composed of columnar and equiaxed crystals that were similar to experimentally observed one.

Fundamental and Practical of High-Temperature Oxidation-2 & 3

S. Taniguchi

Bulletin of The Iron and Steel Institute of Japan, **13**, 35- 43 (2008)
Bulletin of The Iron and Steel Institute of Japan, **13**, 88- 95 (2008)

The article aims at explaining briefly fundamental items regarding the high-temperature oxidation of metallic materials. Practical examples are chosen for deepening the understanding of the readers. This article consists of three parts; part 1 deals with fundamental issues, part 2 includes fundamental issues and oxidation of intermetallic compounds which have been receiving much attention as candidates for heat resisting materials, and part 3 explains a few phenomena encountered in the hot-rolling processes of carbon steels. Part 1 includes relationship between high-temperature structural materials and oxidation, nature and prerequisite of protective oxide scales, thermodynamic considerations, oxidation kinetics in conjunction with crystal defects of oxides and transport phenomena within them, and morphologies of scales together with internal oxidation. (in Japanese)

Interfacial Microstructure of Fe-based Alloys Corroded in Molten Lead-free Solders

A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka

14th Symposium on “Microjoining and Assembly Technology in Electronics”, **14**, 89-94 (2008)

The purpose of the present study is to investigate the effect of alloying elements on the corrosion behavior of Fe-based alloys in molten lead-free solders. Up to 673 K, the corrosion resistances of various stainless steels and Fe-Cr alloys in molten lead-free solder are almost identical. Above 673 K, the corrosion resistance of those alloys depends on the alloying elements, such as C. The presence of carbide in the microstructure may decrease the thickness of consumed substrate. On the other hand, Invar alloys are easily dissoluted above 673 K, resulting in the formation of porous intermetallic layers. Thus, the formation of porous layer promotes inward diffusion of Sn. (in Japanese)

Effects of Additional Elements of Formation of Sub-grain in Sn-based Solder

H. Takaki, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka

19th Symposium of Micro Electronics, 19, 207-210 (2008)

The structural development of Sn grains under stress loading is not well understood yet. In this paper, we observed the macro- and micro structures of the specimens which are loaded during polishing. From the observation of macro structures, it was confirmed that Sn grains grow up to a few millimeters, and from that of micro structures, there exist sub-grains in Sn phase. These growths of the sub-grains would depend on the alloying elements. When the additional elements are Ni, Ge and Cu, the sizes of the sub-grains are nearly equal to those of Sn. In contrast, when additional elements are Al and Bi, the sub-grains become finer. Based on the phase equilibrium diagrams, it can be concluded that sub-grains grows finer when Sn has enough solid solubility of the additional element. (in Japanese)

Effect of Alloying Elements on Corrosion Behavior of Fe-based Alloys.

A. Yamauchi， S. Kawakubo，A. Irisawa，K. Kurokawa and J. Tanaka

19th Symposium of Micro Electronics, 19, 215-218 (2008)

The purpose of this study is to investigate the effect of alloying elements on the corrosion behavior of Fe-based alloys in molten lead-free solders. It is clear that the thicknesses of consumed substrates decrease with increasing the concentration of alloying element. The presence of inner layer formed between reaction layer and Fe-based substrate suppresses the inward Sn diffusion from solder or outward Fe diffusion from the substrate. (in Japanese)

Behavior of in Vitro, in Vivo and Internal Motion of Micro/Nano Particles of Titanium, Titanium Oxides and Others

F.Watari, S.Abe, C.Koyama, A.Yokoyama, T.Akasaka, M.Uo, M.Matsuoka,
Y.Totsuka, M.Esaki, M.Morita, T.Yonezawa

J.Cera.Soc.Jap.116, 1-5 (2008)

To clarify the effect of micro/nanosizing of materials onto biological organism, the particle size dependence of reaction of cells and tissue as investigated by both biochemical cell functional test and animal implantation test. Especially for nanoparticles the behavior of invasion and internal diffusion inside body was visualized using an XSAM (X-ray Scanning Analytical Microscope). The increase of specific surface area is usually counted as nanosizing effect which causes the enhancement of chemical reactivity and therefore toxicity of materials such as carcinogenicity found in 500 nm Ni particles for the long term implantation in the soft tissue of rat. Even biocompatible materials such as Ti and TiO_2 shows stimulus with the decrease of particle size. They cause phagocytosis to cells and inflammation to tissue when the size of particles is below 3 μm. For the size below 50 nm, they may invade into the internal body through the respiratory or digestive system and diffuse inside body. After compulsory exposure test of 30 nm TiO_2 particles through the respiratory system, the Ti mapping by XSAM showed the internal diffusion inside the whole body. Nanoparticles injected from caudal vein diffused with time course to lung, liver and spleen. The uptake of 30 nm TiO_2 particles through the digestive system and diffusion into these organs was also confirmed. These phenomena observed in biocompatible or bioinert materials are the nonspecific, physical particle and shape effects which occur independent of materials. Nanoparticles might be the objects whose existence has not been assumed by the living body defense system.

Internal diffusion of micro/nanoparticles inside body

Fumio Watari, Shigeaki Abe, Kazuchika Tamura, Motohiro Uo, Atsuro Yokoyama, and Yasunori Totsuka

Key Engineering Materials, **361-363**, 95-98 (2008)

Both biochemical cell functional test and animal implantation test were done to investigate the reaction to fine particles. Particles cause nonspecifically phagocytosis to cells and inflammation to tissure for the size below 10 µm. With the size below 50 nm particles may invade into the internal body through the respiratory or digestive system and diffuse inside body. Ti mapping by XSAM after the compulsory exposure test to the respiratory system showed the internal diffusion of 30 nm TiO_2 particles. They diffused with time course to lung, liver and spleen after injection from caudal vein. Nanoparticles might be the objects whose existence has not been assumed by the biophylactic system.

XAFS analysis of Ti and Ni dissolution from pure Ti, Ni-Ti alloy, and SUS304 in soft tissues

Motohiro Uo, Kiyotaka Asakura, Kazuchika Tamura, Yasunori Totsuka, Shigeaki Abe, Tsukasa Akasaka and Fumio Watari

Chemistry Letters, **37**, 958-959 (2008)

Ti, a Ni-Ti alloy, and stainless steel (SUS304) were implanted in rat soft tissues for 6 months. The chemical states of the component elements contained in the tissues surrounding those metallic implants were analyzed by fluorescence X-ray absorption fine structure (XAFS). Titanium oxide and a nickel aquo complex, which would be caused by the erosion of Ti and Ni, were detected in the surrounding tissues. The concentrations of Ti and Ni in the tissues were 1-3 and 300 ppm, respectively. Thus, the dissolved conditions and concentrations of those practical metallic materials in vivo were successfully confirmed.

Carbohydrate Coating of Carbon Nanotubes for Biological Recognition

T. Akasaka and F. Watari

Fullerenes, Nanotubes, and Carbon Nanostructures, **16**, 114-125 (2008)

We have demonstrated that multi-walled carbon nanotubes (MWNTs) coated with a carbohydrate-carrying polymer for use as biological recognition signals can be easily prepared by a non-covalent method via hydrophobic interactions. Fluorescence observation by confocal laser scanning microscopy showed that the carbohydrate-carrying polymers were densely localized around the MWNTs. To evaluate biological recognition affinity, interactions of the MWNTs with lectins were examined by binding tests. The resultant MWNTs were found to acquire a selective binding affinity to the corresponding lectin without a non-specific interaction. On the other hand, bare MWNTs non-specifically interacted with lectins. These results showed that the MWNTs coated with a carbohydrate-carrying polymer have biological recognition signals. Modification of carbon nanotubes with various carbohydrate chains will be a useful protocol for molecular designs of biomaterials, nanoarchitecture and biosensors.

Behavior of in vitro, in vivo and internal motion of micro/nano particles of titanium, titanium oxides and others

Fumio Watari, Shigeaki Abe, Chika Koyama, Atsuro Yokoyama, Tsukasa Akasaka, Motohiro Uo, Makoto Matsuoka, Yasunori Totsuka, Mitsue Esaki, Manabu Morita and Tetsu Yonezawa

J. Ceramic Society of Japan, **116**, 1-5 (2008)

To clarify the effect of micro/nanosizing of materials onto biological organism, the particle size dependence of reaction of cells and tissue as investigated by both biochemical cell functional test and animal implanation test. Especially for nanoparticles the behavior of invasion and internal diffusion inside body was visualized using an XSAM (X-ray Scanning Analytical Microscope). The increase of specific surface area is usually counted as nanosizing effect which causes the enhancement of chemical reactivity and therefore toxicity of materials such as carcinogenicity found in 500 nm Ni particles for the long term implantation in the soft tissue of rat. Even biocompatible materials such as Ti and TiO_2 shows stimulus with the decrease of particle size. They cause phagocytosis to cells and inflammation to tissue when the size of particles is below 3 μm. For the size below 50 nm, they may invide into theinternal body through the respiratory or digestive system and diffuse inside body. After compulsory exposure test of 30 nm TiO_2 particles through the respiratory system, the Ti mapping by XSAM showed the internal diffusion inside the whole body. Nanoparticles injected from caudal vein diffused with time course to lung, liver and spleen. The uptake of 30 nm TiO2 particles through the digestive system and diffusion into these organs was also confirmed. These phenomena observed in biocompatible or bioinert materials are the nonspecific, physical particle and shape effects which occur independent of materials. Nanoparticles might be the objects whose existence has not been assumed by the living body defence system.

Ab-initio calculations on the structures and electronic states of dimethylsulfide-water clusters

Shigeaki Abe, Takahiro Fukuzumi and Hiroto Tachikawa

Synth. React. Inorg. Met.-Org. Nano-Metal Chem., **38**, 105-110 (2008)

Ab initio and density functional theory (DFT) calculation have been applied to hydration processes of dimethylsulfide (DMS), which plays an important role in cloud condensation nuclei (CCN) in marine boundary layer. The molecular complexes composed of water and dimethylsulfide, DMS(H_2O)$_n$ (n=0-3), were examined in the present calculations. The MP4SDQ/6-3-11G(2d,p)//B3LYP/6-31 1D(d,p) calculation indicated that the binding energy of H_2O to DMS is calculated to be 7.7 kcal/mol for n=1. The second water molecule is bound to H_2O of DMS(H_2O) was calculated to be 10.4 kcal/mol. This energy is larger than that of water dimmer (the corresponding binding energy was 6.6 kcal/mol in water dimmer). Direct molecular orbital-molecular dynamics (MO-MD) calculations were carried out for the hydration reactions DMS(H_2O) + H_2O → DMS(H_2O)$_2$ (1) and $H_2O + H_2O \rightarrow (H_2O)_2$ (2) at thermal collision energy. The calculations showed that water dimmer formation reaction on DMS, reaction (1), is efficiently occurred, whereas half of the trajectories for reaction (2) gave dissociation products (H_2O + H_2O). The mechanism of hydration of DMS was discussed on the basis of theoretical results.

The effect of calcium phosphate microstructure on bone-related cells in vitro

XM.Li, CA.Van Blitterswijk, QL.Feng, FZ.Cui, F.Watari

Biomaterials 29, 3306-3316 (2008)

Microstructure is essential for inductive bone formation in calcium phosphate materials after soft tissue implantation. We hereby evaluated activities (cell attachment, proliferation, ALP/DNA and protein/DNA) of three types of cells cultured on three kinds of calcium phosphate ceramic discs to study how microstructure takes its role in inductive bone formation. Three kinds of biphasic calcium phosphate (BCP) ceramic discs with the same chemistry and the same dimension of $10.0 \times 1.0\ \mathrm{mm}^3$ (BCP1150-P, BCP1150-D and BCP1300), either having similar micropore sizes and surface roughness but different surface area (BCP1150-P vs BCP1150-D) or having similar surface area but different micropore sizes and different roughness (BCP1150-D vs BCP1300), were prepared. Conventionally Culturing C2C12, human bone marrow stromal cells (HBMSC) and MC3T3-E1 cells on BCP discs showed that, surface roughness did not affect cell attachment, cell proliferation and ALP expression of all cell types evaluated, while surface area did affect cell functions. ALP/DNA of C2C12 on BCP1150-P, having larger surface area, was significantly higher than on BCP1300 and BCP1150-D. Furthermore, all cells cultured on all of the three kinds of BCPs pre-soaked in culture medium having additional rhBMP-2 had a higher ALP expression than the conventional cell culture. Comparing with on BCP1300 and BCP1150-D, ALP/DNA of all cells tested increased more on BCP1150-P after the discs were pre-soaked in culture medium with rhBMP-2. The results indicated that increasing surface areas, microstructured calcium phosphate materials might concentrate more proteins (including bone-inducing proteins) that differentiate inducible cells to osteogenic cells that form inductive bone.

Preparation and Characteristics of a binderless carbon nanotube monolith and its biocompatibility

Wang, W., Yokoyama, A., Liao, S., Omori, M., Zhu, Y., Uo, M., Akasaka, T., and Watari, F.

Mat. Sci. Eng. C. **28**, 1082-1086 (2008)

A carbon nanotube (CNT) monolith without any binders was obtained by spark plasma sintering (SPS) treatment at 1100 °C under 40 MPa pressure. Transmission electron microscope results confirmed that this material maintained the nanosized tube microstructure of raw CNT powder after SPS treatment. The density and mechanical properties of this material were similar to cancellous bone. The material was implanted in subcutaneous tissue and femurs of rats and tissue samples were analyzed by histopathology at 1 and 4 weeks after surgery. Although some foreign body giant cells were seen around the CNTs, no severe inflammatory response such as necrosis was observed, and CNT implants were surrounded by newly formed bone in the femur. The study provides the first in vivo testing evidence that pure bulk carbon nanotubes are not a strongly inflammatory substance and have no toxicity for bone regeneration. Our study is the first successful experiment to consolidate CNTs without binders, and may provide an effective method for CNT monolith synthesis, as well as demonstrating that a binderless carbon nanotube material with a strength matching that of bone could be a candidate bone substitute material and a bone tissue engineering scaffold material.

Water Corrosion Resistance of ODS Ferritic-Martensitic Steel Tubes

T. Narita, S. Ukai, T. Kaito, S. Ohtsuka and Y. Matsuda

J. Nucl. Science and Technol., **45**, 99–102 (2008)

9Cr- and 12Cr-ODS ferritic-martensitic steels have superior water-corrosion resistance at 333K for 1,000 h under pH values of 8.4, 10, and 12. Thus, it is considered that 9Cr- and 12Cr -ODS claddings keep their strength and are comparable to that of conventional austenitic stainless steel and ferritic-martensitic stainless steel claddings in consideration of the spent-fuel-pool cooling condition.

Precipitation behavior of oxide particles in mechanically alloyed powder of oxide-dispersion-strengthened steel

H. Sakasegawa, M. Tamura, S. Ohtsuka, S. Ukai, H. Tanigawa, A. Kohyamae
and M. Fujiwara

J. Alloys and Compounds, **452**, 2–6 (2008)

The precipitation behavior of oxide particles in mechanically alloyed powder of oxide-dispersion-strengthened steel was studied using chemical extraction method and X-ray diffraction analysis. In particular, the temperature and time dependences of the precipitation behavior of Y–Ti–O oxide particles were investigated. The results suggest more appropriate hot extrusion conditions to finely disperse oxide particles, to improve, and to guarantee the creep property of oxide-dispersion-strengthened steel.

Creep constitutive equation of dual phase 9Cr-ODS steel

H. Sakasegawa, S. Ukai, M. Tamura, S. Ohtsuka, H. Tanigawa, H. Ogiwara, A. Kohyama and M. Fujiwara

J. Nucl. Mater., **373**, 82–89 (2008)

9Cr-ODS (oxide dispersion strengthened) steels developed by JAEA (Japan Atomic Energy Agency) have superior creep properties compared with conventional heat resistant steels. The ODS steels can enormously contribute to practical applications of fast breeder reactors and more attractive fusion reactors. Key issues are developments of material processing procedures for mass production and creep life prediction methods in present R&D. In this study, formulation of creep constitutive equation was performed against the backdrop. The 9Cr-ODS steel displaying an excellent creep property is a dual phase steel. The ODS steel is strengthened by the d ferrite which has a finer dispersion of oxide particles and shows a higher hardness than the a0 martensite. The d ferrite functions as a reinforcement in the dual phase 9Cr-ODS steel. Its creep behavior is very unique and cannot be interpreted by conventional theories of heat resistant steels. Alternative qualitative model of creep mechanism was formulated at the start of this study using the results of microstructural observations. Based on the alternative creep mechanism model, a novel creep constitutive equation was formulated using the exponential type creep equation extended by a law of mixture.

High-Temperature Strength Characterization of Advanced 9Cr-ODS Ferritic Steels

S.Ukai, S.Ohtsuka, T.Kaito, H.Sakasegawa, N.Chikata, S.Hayashi and S.Ohnuki

Proc of Creep and Fracture of Engineering Materials and Structures, Germany, May 4-9, 2008

Oxide dispersion strengthened (ODS) ferritic steels, which are the most promising candidate materials for advanced fast reactor fuel elements, have exceptional creep strength at 973 K. The superior creep property of 9Cr-ODS ferritic steels is ascribed to the formation of a nonequilibrium phase, designated as the residual ferrite. The yield strength of the residual ferrite itself has been determined to be as high as 1360 MPa at room temperature from nanoindentation measurements. The creep strength is also enhanced by minimizing the number of packet boundaries induced by the martensitic phase transformation. The creep strain occurs at a lower stress than that necessary for the deformation of the intragrain regions, which are strengthened by an interaction between nanosize oxide particles and dislocations; this occurs by sliding at weaker regions such as at the grain boundaries and packet boundaries. It is found that 9Cr-ODS ferritic steels behave as fiber composite materials comprising the harder residual ferrite and the softer tempered martensite.

Formation of Ultrafine Grains in 9Cr-ODS Ferritic Steel

N. Chikata, S. Hayashi, S. Ukai, S.Ohnuki, S. Ohtsuka and T. Kaito

Proc of Heat Treatment and Surface Engineering, 557-560 (2008)

The high-temperature strength of 9Cr-ODS ferritic steel (Fe-9Cr-0.13C-2W-0.2Ti -0.35Y_2O_3) is worldwide the most superior in the class of ferritic tubes. This is owing to the unique structure, which was designated as the "*residual ferrite*" by authors. The residual ferrite is generated through pinning of alpha/gamma interfaces by nano-oxide particles during the alpha to gamma reverse phase transformation. In this study, to elucidate the performance in the enhanced strength of 9Cr-ODS ferriteic steel, the mechanical property and structure of the residual ferrite itself are investigated in a nano-micro scale by using nanoindentation hardness tester and transmission electron microscope (TEM). The macro-scopic hardness of 9Cr-ODS ferritic steel is proportional to the volume fraction of existing residual ferrite. This result coincides with the creep rupture strength. The proper nano-scopic hardness corresponding to individual phase of the residual ferrite and martensite was measured by nano-indentation at the condition of the normalizing and tempering. Nano-hardness of the martensite reduces with increasing tempering temperature, whilst the residual ferrite maintains higher level of nano-hardness. TEM observation confirmed that the residual ferrite contained ultrafine grains. From the selected area diffraction (SAD) study with TEM, the residual ferrite comprises ultrafine grains of 500 nm in size, whilst the tempered martensite is decomposed to ferrite phase in the grain size of 2.5 μm. Based on the Hall-Petch relationship, the yield stress of the residual ferrite is approximately 500 MPa higher than that of the tempered martensite. It is concluded that extremely high nano-hardness and high yield stress in the residual ferrite are attributed to the grain refinement strengthening by the ultrafine grains.

Decomposition-Precipitation Behavior of Oxide Particles in Ni nano-Crystals

T. Hoshino, S. Hayashi and S. Ukai

Proc of Heat Treatment and Surface Engineering, 643-646 (2008)

Recently, the high-temperature strength of Fe-based ODS ferritic steels has been dramatically improved through introducing nano-size oxide particles by one of the authors. For the purpose of improving the high-temperature strength of Ni-base ODS superalloys, we promoted to make ultrafine nano-size dispersion of the oxide particles, because the commercialized one contains Y-Al oxide particles in the size of several ten nano-meter. As the first step of this study, the morphology change of Y_2O_3 oxide particles and related phenomena of Ni alloy matrix were investigated by means of mechanical alloying (MA) and subsequent heat treatment. The Ni-10Y_2O_3, Ni-1Y_2O_3 and Ni-0.5Al-1Y_2O_3 (mass %) powders were mechanically alloyed for max 100h by using planetary type of ball-mill. Subsequent heat treatment was conducted at temperature ranging 373K-1673K. XRD and hardness measurement were performed in as-MA and heat treated powders. Some of MA powders were hot-pressed at 1473K and 57MPa for 3h, and TEM analysis was performed using their thin foil specimens prepared by electrolytic polishing. The grain size of Ni matrix is extremely reduced to 50 nm in nano-size, and Y_2O_3 particles are concomitantly decomposed during initial stage of mechanical alloying of 3-10h. The subsequent heat treatment at temperature beyond 873K induces re-precipitation of Y_2O_3 oxide particles. The nanocrystalline structure of Ni -10Y_2O_3 was maintained until coarsening of oxide particles that leads to decrease of pinning force for recrystallization over temperature of 1573K. The mean size of oxide particle is 14 nm for Y_2O_3 (Ni-1Y_2O_3) and 16 nm for Y-Al oxide (Ni-0.5Al -1Y_2O_3). Both are almost similar in size, and larger than that of ODS ferritic steel of 5nm.

The Effect of Additional Elements on Oxide Scale Evolution of Fe-20%at.Cr-10at.%Al alloy at 900 ° C in air

Y. Kitajima, S. Hayashi, S. Ukai, and T. Narita

Mater. Sci. Forum, 595-598, 1013-1021 (2008).

The oxidation behavior of Fe-20at.%Cr-10at.%Al alloys with a small amount of an additional element such as W, Cu, Mn, Nb, Mo, Re, Co or Ti was investigated at 900 ºC for up to 625hr. The fourth element addition to the FeCrAl alloy could be classified into two groups; elements (Mn, Nb, Ti) that are contained in the Al_2O_3 scale, and elements (W, Mo, Re, Co) which are not present in the scale. In the latter case, the elements (W, Cu) caused scale spallation. The rumpling of alloys with Mn, Nb or Ti was smaller than that of the other alloys. The surface of the alloy with Ti was the smooth. Pt marker experiments suggested that the Al_2O_3 scale formed on the alloy with Ti grew by inward diffusion of O, whilst the Al_2O_3 scale formed on the FeCrAl alloy grew by both outward diffusion of Al and inward diffusion of O. This different growth behavior due to the elements incorporated in the Al_2O_3 scale could have an effect on the surface rumpling behavior.

Formation of Pt-modified γ'-Ni_3Al and Re-Based σ-Alloy Coating System and Cyclic Oxidation Behavior of Coated Superalloy

T. Narita, S. Ford, T. Yoshioka, T. Nishimoto, T. Izumi, and S. Hayashi,

Mater. Sci. Forum, 595-598, 135-141 (2008).

A duplex layer, outer Pt-modified γ'-Ni3Al + γ-Ni and inner multi-barrier σ-Re(Cr,Ni,W), coating system was formed on a Ni-based single crystal 4th generation superalloy. Oxidation behavior of the coated alloy was investigated under thermo-cycling conditions, and analyzed by EPMA and XRD. During cyclic oxidation 1hr at 1100°C and 20 min at room temperature, a slow growing α-Al_2O_3 formed for up to 400 cycles and its spallation was rare. The parabolic rate constant of mass change was 6.3x10-16 $kg^2m^{-4}s^{-1}$. The Pt-modified γ'-Ni_3Al + γ-Ni contained 19Al, 12Pt, 4Cr, and 3Co in at%, and their concentration profiles were almost flat across the outer layer. The multi-barrier, σ-Re(Cr,Ni,W) contained 40Re, 23Cr, 17Ni, 7Al, 4W, 3.5Mo, and 3Co in at%. Furthermore, the γ'-Ni_3Al containing Pt was newly formed between the multibarrier and bulk alloy substrate. It was concluded that the σ-Re(Cr,Ni,W) is compatible with the Ptmodified γ'-Ni_3Al in the multi-diffusion barrier coating on Ni-based single crystal, 4th generation superalloy at high temperatures.

Creep Deformation/Oxidation Behavior of Re-Cr-Ni Diffusion Barrier Coated Hasetelloy-X at 970 ° C in Air

S. Hayashi, M. Sakata, S. Ukai, and T. Narita, ,

Mater. Sci. Forum, 595-598, 107-116 (2008).

High temperature oxidation / creep deformation behavior of a diffusion barrier coated Hastelloy-X alloy, with large grain size ~500μm, was investigated at 970ºC in air with external tensile stress of 22.5, 27.5, 32, and 40MPa. The diffusion barrier coating formed on Hastelloy-X consisted of a duplex structure with an inner diffusion barrier layer of Re-Cr-Ni alloy, and an outer oxidation resistant layer of β-NiAl. Un coated bare Hastelloy-X alloy with same grain size was also examined under the same conditions for comparison. The composition of the as-coated diffusion barrier coating was (15~21)Ni, (33~37)Cr, (30~33)Re, (11~15)Mo, and (9~14)Fe. This composition corresponds to σ-phase in the Ni-Cr-Re ternary system, which is known as a topologically close packed, TCP phase. The composition of this diffusion barrier layer did not change during the experiment. The oxide scales formed after creep testing on the coated and un-coated alloy surfaces were needle-like θ-Al_2O_3, and Cr_2O_3 with small amount of $FeCr_2O_4$, respectively. Grain boundary oxidation was also found in the subsurface region of the un-coated alloy. The Al_2O_3 scale exhibited severe spallation, and many cracks were formed perpendicular to the stress direction. However, no spallation or cracks were observed in the Cr_2O_3. The creep rupture times for the diffusion barrier coated alloy were about 1.5 times longer than those for bare alloy at all creep stress conditions. The fracture surface after rupture indicates that fracture occurred along alloy grain boundaries in both the coated and un-coated alloy substrate. Many cavities and cracks were observed within the diffusion barrier coated alloy substrate. These cavities and cracks tended to propagate from the substrate toward the diffusion barrier layer, and then stopped at the Re-Cr-Ni / β-NiAl interface. Cracks formed in the un-coated alloy initiated at the tip of grain boundary oxides, and propagated into alloy substrate. However no major cavities were observed inside the alloy substrate. The stress index, n, for both specimens was about 6, and this indicates that the deformation mechanism of both samples was dislocation creep. These results suggest that the Re-Cr-Ni diffusion barrier layer acts as a barrier against the movement of dislocations at the interface with the alloy surface.

Platinum Diffusion and Microstructure Change in a Single Crystal Superalloy and Nickel-based Model Alloys at 1000 ° C

S. Ford, S. Hayashi, and T. Narita,

Mater. Sci. Forum, 595-598, 69-76 (2008).

Single crystal superalloy TMS82+ and model alloys of Ni-12Al and Ni-6Cr-8Co-12Al were electroplated with 5-6μm of platinum and heat treated at 1000.C for up to 100hrs. In the model alloys the platinum concentration gradient in the interdiffusion region caused uphill diffusion of aluminium. The subsequent surface enrichment led to formation of aluminium-rich γ' phase. In TMS82+ superalloy inward diffusion of platinum resulted in loss of the γ/γ' microstructure and formation of new γ and γ' grains. The initial dissolution of the γ' cubes was due to the outward diffusion of aluminium. Again, the presence of a platinum gradient in the interdiffusion region resulted in uphill diffusion of aluminium and a net increase in aluminium content at the alloy surface, leading to a near-surface single-phase γ' layer being formed, however topologically close-packed (TCP) phase formation was not observed.

Interdiffusion in Pt-Containing γ -Ni and γ '-Ni3Al Alloys at 1150 ° C

S. Hayashi, D.J. Sordelet, L.R. Walker and B. Gleeson,

Materials Trans., 49, 1550-1557 (2008).

Ternary interdiffusion coefficients in the γ-Ni and γ'-Ni3Al phases of the Ni-Al-Pt system at 1150°C were experimentally determined by applying a Boltzmann-Matano method at a common composition in the time-invariant diffusion paths for a given two couples. The variation of the main-term interdiffusion coefficients of Al, $\tilde{D}_{Al,Al}^{Ni}$, with increasing of Pt content was different for the γ and γ' phases. In γ $\tilde{D}_{Al,Al}^{Ni}$ generally increased with increasing Pt content, but it decreased with increase in Pt in γ' phase. By contrast, the main-term coefficients for Pt, $\tilde{D}_{Pt,Pt}^{Ni}$, apparently increased monotonically with increasing Pt content in both phases, but there was little dependency on Al content. The cross-term interdiffusion coefficients, $\tilde{D}_{Al,Pt}^{Ni}$ and $\tilde{D}_{Pt,Al}^{Ni}$, were negative in both γ and γ', showing that the chemical interaction between Al and Pt in these phases is negative. $\tilde{D}_{Al,Pt}^{Ni}$ values were larger than those of $\tilde{D}_{Pt,Al}^{Ni}$; however, there was no clear dependence of $\tilde{D}_{Al,Pt}^{Ni}$ and $\tilde{D}_{Pt,Al}^{Ni}$ on Pt and Al contents within the composition ranges studied. The cross-term interdiffusion coefficients were comparable to the main-term coefficients in γ and within an order of magnitude of each other in γ'. The significance of these findings are discussed and quantitatively assessed

Effects of pH and temperature on the deposition properties of stannate chemical conversion coatings formed by the potentiostatic technique on AZ91 D magnesium alloy

H H. Elsentriecy, K. Azumi and H. Konno

Electrochimica Acta, 53, 4267-4275 (2008)

The effects of pH and temperature of a stannate bath on the quality of stannate chemical conversion coatings formed on AZ91D magnesium alloy by using the potentiostatic polarization technique at $E = -1.1$V were investigated in order to improve uniformity and corrosion protection performance of the coating films. It was found that the uniformity and corrosion resistance of coating films deposited by potentiostatic polarization were closely associated with pH and temperature of the coating bath. The pH and temperature to obtain the best coating film were investigated as a function of corrosion protection performance evaluated by curves of potentiodynamic anodic polarization conducted in borate buffer solution. Scanning electron microscope observation and electrochemical corrosion tests of the stannate-coated samples confirmed significant improvement inuniformity and corrosion resistivity of coating films deposited by the potentiostatic technique by modifying the pH and temperature of the coating bath. It was also found that uniformity and corrosion resistivity of the coating films deposited by the potentiostatic technique were considerably improved compared to those of coatings deposited by the simple immersion method at the best conditions of pH and temperature of the coating bath.

Reduction of $TiCl_4$ gas by Ca dissolved in the molten $CaCl_2$

T, Naito, R.O.Suzuki and Y.Tomii

Proc. 11th World Conference on Titanium (Ti-2007), 103-106 (2007)

A new Ti production method was studied. It employs calcium dissolved in molten $CaCl_2$ to reduce the gaseous $TiCl_4$ thermochemically in order to form metallic Ti continuously. The Ca is supplied in-situ by the electrolysis of molten $CaCl_2$. This concept was verified by the experiments that the metallic particles and their sintered powder were recovered from the bottom of the crucible, when Ca was produced three times larger than the theoretical amount for reduction. However, a part of calcium formed by the electrolysis dissolved in $CaCl_2$ and it was reacted with Cl_2 gas that evolved at the anode. $TiCl_4$ gas blown to a position with a low Ca concentration was recovered as the lower oxides of titanium. The conditions suitable for titanium powder production from $TiCl_4$ gas were to supply enough amount of Ca for reduction even if Ca is localized, and to keep a Ca concentration higher than 2 mol%.

Calciothermic Reduction of TiO_2 with ZrO_2 Anode in Molten $CaCl_2$

R.O.Suzuki

Proc. 11th World Conference on Titanium (Ti-2007), 99-102 (2007)

Calciothermic reduction for Ti metal production has been developed, where TiO_2 is reduced by calcium electrochemically deposited and dissolved in molten $CaCl_2$. To prevent carbon contamination in Ti and to improve current efficiency in electrolysis of CaO, a dense yttria stabilized zirconia (YSZ) membrane was experimentally examined. Oxygen and carbon contaminations in Ti were successfully minimized by the YSZ membrane.

Preparation of Hydrogen Storage Ti-V-Cr Alloy from the Oxide Mixture in $CaCl_2$

K. Kanou and R.O.Suzuki

Proc. 11th World Conference on Titanium (Ti-2007), 107-110 (2007)

The mixture of TiO_2, V_2O_3 and Cr_2O_3 powders were reduced simultaneously inside the basket-type of cathode in the molten $CaCl_2$, where the by-product CaO was returned to the reductant Ca by the electrolysis. A fine metallic particles consisting of the BCC solid solution and a small amount of $TiCr_2$ phase were successfully obtained after 10.8 ks at 1173 K. The oxygen concentration was in the level of 2000 mass ppm. The carbon contamination due to CO_2 gas evolution at the anode during the electrolysis could be avoided by the electrode arrangement in the melt. The compositional homogeneity in the sample was improved by the rapid cooling, because the BCC solid solution decomposes during the slow cooling from 1173 K. This sample could absorb about 1.9 mass % hydrogen at maximum, and the effective (reversible) hydrogen storage was 1.68 mass %, which approached to 87.5% of the previous reports.

Direct Reduction of Vanadium Oxide in the Molten Calcium Chloride

Y. Oka and R.O.Suzuki

J. Jpn. Inst. Met. **72**, 181-187 (2008)

A new process is proposed to reduce V_2O_5 by using calcium in molten $CaCl_2$. It consists of the calcium reduction in molten $CaCl_2$ and the electrochemical reaction for the recovery of Ca from CaO in the same bath. V_2O_5 pellet was placed on cathode in order to react with Ca electrochemically generated near the cathode. V_2O_5 exists as liquid at the experimental temperature (1123K), because of the melting point of 963K for V_2O_5. At the initial stage of the reduction, liquid sample was reduced to solid CaV_2O_4. As the supplied quantity of electricity increased, the oxygen concentration in the samples decreased exponentially. Vanadium containing only 1800 ppm oxygen was obtained after the electrolysis for 34.4ks.

Calciothermic Reduction and Simultaneous Electrolysis of CaO in the Molten $CaCl_2$ - Some Modifications of OS Process

R.O.Suzuki

Proc. of 1st Intern. Round Table on Titanium Production in Molten Salts, 20-26 (2008)

The goal of the new process is the conversion of the TiO_2 particles into ductile Ti without contamination by oxygen and carbon, which have an extremely strong affinity to Ti. The new alternative method should possess the same requisites as the Kroll process, in addition to new merits such as continuous operation and good energy efficiency that the Kroll process can not realize. A review on the calciothermic reduction and its application in the molten $CaCl_2$ is described. The principle of OS process is explained in the electrochemical viewpoints, and the combination of electrolysis of CaO and simultaneous reduction of TiO_2 is proposed. Some current researches in my group are overviewed and the possible industrial models are shown. The usage of ceramic membrane is effective to separate the gas bubbles from the cathodic area. The Y_2O_3-stabilized ZrO_2 (YSZ) was excellent because its oxygen ionic conductivity cut off the Ca ion movement through the membrane although the current become 1/5 - 1/10. Solubility analysis of CO_2 in the molten $CaCl_2$ and the trial of $TiCl_4$ reduction are briefly summarized.

Direct Reduction of Vanadium Oxide in Molten $CaCl_2$

R. O. Suzuki and H. Ishikawa

Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C), **117**, 108-112 (2008)

A combined process of electrolysis of CaO in molten $CaCl_2$ and calciothermic reduction, the so called OS process, was applied to prepare metallic vanadium directly from V_2O_3. Fine metallic powder containing 1860 wt ppm oxygen was obtained using a 0.5 mol%CaO–$CaCl_2$ melt following processing for 10.8 ks (3 h) at 1173 K. The oxygen level did not decrease further even when the current was doubled. Because metallic vanadium can be electrochemically deoxidized to 10 ppm oxygen from 1.48%, the high oxygen content in the reduced powder was attributed to the large amount of byproduct CaO, due to reduction and the large surface area of the fine particles.

Influence of Current Density to Direct Reduction of TiO_2 in Molten $CaCl_2$

K. Kobayashi, Y. Oka and R.O.Suzuki

J. Jpn. Inst. Metals, **72**, 916-920 (2008)

TiO_2 was successfully reduced at 1223K by calcium, which was deposited due to the molten salt electrolysis of CaO dissolved in $CaCl_2$. By changing the area of electrodes and the electrodes distances, the current density and the Ca concentration near the cathode were varied, respectively. At the initial stage of reduction, metallic Ti powder with the lower oxygen concentration was obtained at the lower current density, where most of electrochemically deposited Ca was efficiently used for the reduction. Meanwhile, at the final stage of reduction /deoxidation, Ti powder with the much lower oxygen concentration were obtained at the higher current density, where the higher Ca concentration was available near the cathode. In order to obtain the metallic powder with the low oxygen content, the formed Ca can penetrate even into the inner part of the sintered oxide

Synthesis of Ti-6Al-4V Alloy by the Electrolysis of Molten $CaCl_2$+CaO

H. Sakai, Y. Oka and R.O. Suzuki

J. Jpn. Inst. Metals, **72,** 921-927 (2008)

A new process is developed to synthesize the precious alloy directly from the oxide mixtures. This process consists of calciothermic reduction in molten $CaCl_2$ and electrochemical reaction for the recovery of Ca from CaO in the same bath. The molten $CaCl_2$ can dissolve Ca and CaO for complete reaction. The oxide mixture consisting of TiO_2, Al_2O_3, and V_2O_5 was prepared. Either a simple mixture of oxides or its calcined sample was reduced in the molten $CaCl_2$+CaO. The obtained metallic powder was identified as α-Ti single phase and it contained only about 3000 mass ppm oxygen. Although its metallic composition was close to Ti-6Al-4V, this reduced powder had a broad compositional distribution. This inhomogeneous distribution was improved by the subsequent sintering in argon.

Solubility of CO_2 Gas in the Molten CaO-$CaCl_2$

J. Hashizume, Y.Oka and R.O.Suzuki

Proc. 2008 Joint Symp. on Molten Salts (MS8), 128-133 (2008)

Under P_{CO2}=1 atm, the dissolved CO_2 gas in CaO-$CaCl_2$ was analyzed by the mass change in dissolution in HClaq. The solubility of CO_2 gas changed at $N_{CaO}=0.10$. The equilibrium with $CaCO_3$ was suggested at 1123K and $N_{CaO}>0.10$. Additionally, the experimental error was estimated as ±1.6% of the analytical value.

Synthesis of Ti-6Al-4V Alloy Powder by the Electrolysis of Molten $CaCl_2$+CaO

H.Sakai, Y.Oka and R.O.Suzuki

Proc. 2008 Joint Symp. on Molten Salts (MS8), 354-359 (2008)

The oxide mixture of TiO_2, Al_2O_3, and V_2O_5 was reduced in the molten $CaCl_2$+CaO. The obtained metallic powder was identified as α-Ti single phase by X-ray diffraction measurement, and it contained only about 3000 ppm oxygen, which is as low as a commercially pure titanium. The homogeneous distribution of the constitutional elements in SEM observation was achieved by the subsequent sintering in vacuum.

Direct Reduction of Liquid V_2O_5 in Molten $CaCl_2$

Y.Oka and R.O.Suzuki

Proc. 2008 Joint Symp. on Molten Salts (MS8), 655-657 (2008)

The new process is studied using the calciothermic reduction for vanadium production in molten $CaCl_2$. The generated gas concentration was analyzed. At the anode, both CO_2 and CO were evolved as a result of electrolysis CaO. The relationship between the oxygen concentration in the sample and the supplied charge is discussed.

Calciothermic Reduction of $TiCl_4$ Gas by Electrolysis in $CaCl_2$ Melt

R.O.Suzuki and T. Naito

Proc. 2008 Joint Symp. on Molten Salts (MS8), 658-663 (2008)

$TiCl_4$ gas was blown to the melt surface of $CaCl_2$ + Ca, and α-Ti powder was obtained when Ca content was >2.0 mol%. When Ca was produced by the electrolysis of $CaCl_2$, the dendritic Ti was deposited from $TiCl_3$ and/or $TiCl_2$ in addition to the powder. A little amount of oxygen dissolved in the salt formed the titanium suboxides such as Ti_2O and TiO.

Current Density in OS Process for TiO_2 Reduction

K.Kobayashi, Y.Oka and R.O.Suzuki

Proc. 2008 Joint Symp. on Molten Salts (MS8), 742-747 (2008)

TiO_2 was reduced by the molten salt electrolysis in $CaCl_2$. The metallic Ti powder with the lower oxygen content was obtained at the lower current density at the initial stage of reduction, while the lower oxygen content residual in α–Ti solid solution was obtained at the longer electrode distance and the thicker cylindric cathode at the final stage of reduction /deoxidation.

Bonding and Thermal Fracture of Silicon Nitride / Stainless Steel (SUS316)

H. Kiyono, T. Nukui, T. Akashi and S. Shimada

Trans. Mater. Res. Soc. Japan, **33**, 953-956 (2008)

Diffusion bonding and thermal fracture between Si_3N_4 ceramics and stainless steel (SUS316) were investigated. Sintered Si_3N_4 ceramics were fabricated by hot-pressing of α-Si_3N_4 powder with 5wt% Y_2O_3 and 5 – 10wt% Al_2O_3. Bonding between SUS316 plate with 1 mm thick and Si_3N_4 specimens was carried out at 8 – 24 MPa and at 1000 - 1300ºC for 1 h in vacuum. Thermal decomposition of the bonded specimen in air was followed by acoustic emission and high-temperature microscope. Bonding between SUS and Si_3N_4 was achieved by heating at 1150 and 1200ºC in vacuum. When the bonded sample was heated in air, small cracking was formed at 700ºC at the interface between SUS and Si_3N_4, followed by decomposition of the bonded sample at 900ºC.

SIMS Study of SiC Single Crystal Oxidized in Atmosphere Containing Isotopic Water Vapor

T. Akashi, M. Kasajima, H. Kiyono and S. Shimada

J. Ceram. Soc. Japan, **116**, 960-964 (2008)

Double oxidation of SiC single crystal was carried out in oxidizing gas (O_2 or H_2O) at 1673 K first and then in isotopic water ($H_2{}^{18}O$ or D_2O) at 1473 K or 1573 K to trace diffusing species during oxidation at high temperatures. SIMS analysis revealed that deuterium was enriched near SiO_2/SiC interface when SiC was oxidized in Ar/D_2O gas mixture at the second oxidation step, indicating that water molecules or hydroxyls diffused in SiO_2 layer to the SiO_2/SiC interface. Large amount of carbon in SiO_2 scale near the SiO_2/SiC interface after oxidation in dry Ar/O_2 gas mixture suggests a possibility that outward diffusion of carbonaceous species can be rate-controlling step during oxidation in dry Ar/O_2 atmosphere. Decrease in the amount of the carbon with oxidation time in Ar/$H_2{}^{18}O$ gas mixture at the second oxidation step implies that the outward diffusion of carbonaceous species in SiO_2 scale was promoted during oxidation in atmosphere containing water vapor.

Development of a novel microstructure fabrication method with co-axis dual capillary solution flow type droplet cells and electrochemical deposition

M. Sakairi, F. Sato, Y. Goto, K. Fushimi, T. Kikuchi and H. Takahashi;

Electrochimica Acta, **54**, 616-622 (2008).

A new method for maskless fabrication of metallic patterns or structures on metals is described. A solution flow type droplet cell, with co-axial dual capillaries was applied to form fine metal structures such as strips and rods. This type of droplet cell enables movement of the cell during formation. Nickel fine patterns with a width of about 200 μm were formed on a Cu substrate. The width of the formed pattern does not change with the scanning speed of the cell, but the thickness of the formed pattern changes with the speed. Two different deposition modes were examined to form metal rods, one is a mold free deposition mode and the other is a mold assisted deposition mode. Both modes enable the formation of Ni rods, however, reproducibility of mold free deposition mode was not good. The mold assisted deposition mode has far better the reproducibility, because of the use of the inside wall of the 100 μm diameter inner tube as the mold. It is possible to form nickel micro-rods, about 100 μm in diameter and 12 mm long with relatively smooth surfaces by the mold assisted deposition mode.

Hydrogen Absorption into Anodized Niobium Electrodes during Cathodic Polarization

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J. Surf. Finish. Soc. Jpn, **59**, 326-332 (2008).

Cathodic polarization of niobium specimens that have been anodized galvanostatically up to $E_a = 100$ V, and then potentiostatically at $E_a = 100$ V has been investigated in a neutral borate solution. During potetiostatic cathodic polarization below $E_c = -2.36$ V (vs. RHE) in both aerated and deaerated solutions, the cathodic current increased rapidly initially, and then increased gradually until it reached a steady value. Hydrogen gas evolution was observed during cathodic polarization below $E_c = -2.36$ V with no formation of blisters and pits, suggesting that H^+ reduction occurs mainly at the film surface. GD-OES spectra revealed that hydrogen species are enriched in the niobium substrate near the interface between anodic oxide films and the substrate at potentials below $E_c = -2.36$ V, and that the trend is pronounced at lower potentials. Chemical shift was observed on Nb 3d and O 1s peaks in XPS spectra for the specimen at $E_c = -3.36$ V, suggesting the formation of $Nb_2O_3(OH)_2$. Mechanism for the reaction during cathodic polarization in a neutral solution is discussed in terms of the proton reduction at the interfaces both between oxide films / solutions and between oxide films / substrates. (in Japanese)

Reactivity imaging of a passive ferritic steel

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J. Appl. Electrochem., **38**, 1339-1345 (2008).

A technique named reactivity imaging is introduced. It combines optical imaging of a polycrystal- line material with orientation imaging by electron back scattering diffraction (EBSD) for a determination of the crystallographic orientation map and scanning electrochemical microscopy (SECM) for a visualization of the local reactivity. Dissolving metal ions from the substrate are directly detected by the scanning Pt tip of the SECM to measure the amount of locally dissolving material. A ferritic light weight steel (alloy Fe7.5Al7Cr) with a strong anisotropic dissolution behaviour was investigated as an example. This steel shows good passivation behaviour both, in air and through anodisation. In the passive state investigated here, the difference in dissolution rate between various crystallographic orientations is only marginal. Grain boundaries on the other hand showed a higher activity as compared to the grains themselves, which is attributed to the electronic tunnelling in the grain boundaries. The results demonstrate that the rate determining step responsible for the anisotropic dissolution does not result from a deficiency in passivation but from the active dissolution kinetics.

Anodic Dissolution of Titanium in NaCl-containing Ethylene Glycol

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Electrochimica Acta, **53**, 3371-3376 (2008).

Anodic dissolution behavior of titaniumin NaCl-containing ethylene glycol has been examined to obtain electropolished titanium surface. During anodic polarization in 1 mol dm^{-3} NaCl ethylene glycol solution at 293K, the titanium electrode covered with oxide dissolves with gas evolution at potentials higher than 10 V (Ag/AgCl) while it is in passive state at potentials lower than 5 V. However, after removal of the oxide layer by pre-polarization at gas-evolving potentials, no gas evolution is observed, and the titanium electrode shows a limiting dissolution current as tetravalent species at potentials higher than 5 V, producing a smooth surface. The polarization of the rotating disk titanium electrode reveals that the kinetics of the mass transfer reaction for electropolishing of titanium is controlled by titanium species dissolved into the solution, not by chloride ions or water containing in the solution. Repetition of dynamic polarization gives a well-electropolished surface.

Current Distribution during Galvanic Corrosion of Carbon Steel Welded with Type-309 Stainless Steel in NaCl Solution

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Corrosion Science, **50**, 903-911 (2008).

Galvanic corrosion of carbon steel welded with type-309 stainless steel in NaCl solution was tentatively evaluated with a newly developed multi-channel electrode technique in which the welded specimen was divided into nine working electrodes (WEs), reconstructed in resin, and connected individually to an imaginary ground level of an electric circuit via relay switches. This allows the WEs to join a galvanic couple and simultaneous measurement of participating current or open circuit potential of each WE. WEs were immersed together in 5.1 x 10^{2} mol dm^{-3} or 2.1 x 10^{-4} mol dm^{-3} NaCl solutions, and spatial distribution of participating currents and open circuit potentials were monitored as a function of immersion time. The WE of the weldment acted as a cathode throughout the immersion period, while the other WEs of base steel became anodes or cathodes depending on their location, immersion time and concentration of the electrolyte solution. The ability of zinc-rich paint to protect the welded specimen as sacrificial anode was also investigated.

Cross-section Corrosion-potential Profiles of Aluminum-alloy Brazing Sheets Observed by the Flowing Electrolyte Scanning-droplet-cell Technique

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Electrochimica Acta, **53**, 2529-2537 (2008).

The scanning-droplet-cell (SDC), recently used for studying electrochemistry of electrodes in micro-areas, was modified to a flowing electrolytetype one (f-SDC), in which fresh electrolyte was continuously supplied on the surface to be examined. The f-SDC with a coaxial double capillary structure could avoid the contamination of electrolyte by species dissolved from the measuring electrode surface. In the present study, the f-SDC technique was applied successfully to obtain profiles of the corrosion potential for the cross-sections of aluminum-alloy brazing sheets, used for the heat exchanger of the automobile. The brazing sheets consist of an Al–Zn alloy sacrificial anode layer, an Al–Mn–Cu core layer and an Al–Si brazing filler. The profiles of the corrosion potential, important to evaluate the corrosion protection performance of the sacrificial anode, revealed that the potential gradient arising from the sacrificial anode to the core layer is mainly controlled by zinc, which diffuses from the former layer to the latter during the cladding treatment and the post-heat treatment.

Electrochiemical behavior of low C-13%Cr weld joints by using solution flow type micro-droplet cell

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Proc. of NACE2008, No. 08102 (2008)

Low Carbon-13%Cr martensitic stainless steels have been widely used for line pipe application because of their high strength and excellent corrosion resistance in corrosive conditions. Recently, both laboratory and field experiences related to cracking near fusion line of these steels weld joints in hot acid environments has been published. Electrochemical analysis of weld joints are expected to be effective to understanding crack mechanism. In this paper, electrochemical behavior of low C – 13%Cr weld joints was measured by using solution flow type micro-droplet cell. In this unique technique, a droplet with a diameter of hundreds of micrometers is used as an electrochemical cell and this technique enables local electrochemical measurements. Measurement of corrosion potentials and potentiodynamic polarization for HAZ portion of weld joints were focused.

Synthesis of aluminum oxy-hydroxide nanofibers from porous anodic alumina

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Nanotechnology, **19**, 395603-395608 (2008)

A novel method for the synthesis of aluminum oxy-hydroxide nanofibers from a porous anodic oxide film of aluminum is demonstrated. In the present method, the porous anodic alumina not only acts as a template, but also serves as the starting material for the synthesis. The porous anodic alumina film is hydrothermally treated for pore-sealing, which forms aluminum oxy-hydroxide inside the pores of the oxide film as well as on the surface of the film. The hydrothermally sealed porous oxide film is immersed in the sodium citrate solution, which selectively etches the porous aluminum oxide from the film, leaving the oxy-hydroxide intact. The method is simple and gives highly uniform aluminum oxy-hydroxide nanofibers. Moreover, the diameter of the nanofibers can be controlled by controlling the pore size of the porous anodic alumina film, which depends on the anodizing conditions. Nanofibers with diameters of about 38–85 nm, having uniform shape and size, were successfully synthesized using the present method.

Electrochemical random signal analysis during localized corrosion of anodized 1100 aluminum alloy in chloride environments

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Corrosion Scinece and Technology, **7**, 168-172 (2008)

A new type of electrochemical random signal (electrochemical noise) analysis technique was applied to localized corrosion of anodic oxide film formed 1100 aluminum alloy in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.01 kmol/m^3 NaCl. The effect of anodic oxide film structure, barrier type, porous type, and composite type on galvanic corrosion resistance was also examined. Before localized corrosion started, incubation period for pitting corrosion, both current and potential slightly change as initial value with time. The incubation period of porous type anodic oxide specimens are longer than that of barrier type anodic oxide specimens. While pitting corrosion, the current and potential were changed with fluctuations and the potential and the current fluctuations show a good correlation. The records of the current and potential were processed by calculating the power spectrum density (PSD) by the Fast Fourier Transform (FFT) method. The potential and current PSD decrease with increasing frequency, and the slopes are steeper than or equal to minus one (-1). This technique allows observation of electrochemical impedance changes during localized corrosion.

Galvanic corrosion of anodized aluminum -Influence of anodic oxide film structure and concentration of Cl^-

M. Sakairi, Y. Shimoyama, D. Nagasawa, T. Kikkuchi and H. Takahashi

Zairyo-to-Kankyo, **57**, 194-200 (2008)

The effect of anodic oxide film structure, barrier type and porous type on galvanic corrosion resistance of aluminum in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ with NaCl was examined by electrochemical random signal (electrochemical noise) analysis technique. When pitting corrosion occurs, rest potential suddenly decreases and current increases rapidly, and rest potential and current change with fluctuation during galvanic corrosion. The galvanic current change correlates closely with corrosion potential change. As the thickness of both types of anodic oxide films and decreasing of chloride ion concentration, the incubation time of pitting corrosion became longer, and incubation time of pitting corrosion of specimen formed porous type anodic oxide film is longer than that of specimen formed barrier type anodic oxide film. The inverse of incubation time increase with chloride ion concentration to the power of n, $[Cl^-]^n$. The value of n is between 1.2 and 2.5 in both oxide films. (in Japanese)

Influence of Zinc ions on initial stage of localized corrosion of Zn and Zn-Al alloy coated steels with photon rupture method

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ISIJ Int., **48**, 988-993 (2008)

The effect of pre-dissolved Zn ions in the solutions on the initial stage of localized corrosion after oxide films of Zn and Zn-Al alloy coated steels were removed by a photon rupture method, focused pulsed Nd - YAG laser beam irradiation, was investigated electrochemically. Zn ions can be inhibited dissolution of the Zn coated layer by precipitation of zinc hydroxide, which is formed by hydrolysis reaction of dissolved Zn ions in neutral buffer solutions. However, Zn ions do not affect the dissolution of a Zn-Al alloy coated layer. The absence of inhibition of the Zn-Al layer dissolution can be explained by pH change to lower values at the irradiated area by the hydrolysis reaction of the dissolved Al ions. The effect of Zn ions on corrosion inhibition of the coated layer by the photon rupture method established here was in good agreement with polarization experiments.

Fabrication of micro-dot arrays and micro-walls of acrylic acid/melamine resin on aluminum by AFM probe processing and electrophoretic coating

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Electrochimica Acta, **53**, 8118-8127 (2008)

Micro-dot arrays and micro-walls of acrylic acid/melamine resin were fabricated on aluminum by anodizing, atomic force microscope (AFM) probe processing, and electrophoretic deposition. Barrier type anodic oxide films of 15 nm thickness were formed on aluminum and then the specimen was scratched with an AFM probe in a solution containing acrylic acid/melamine resin nano-particles to remove the anodic oxide film locally. After scratching, the specimen was anodically polarized to deposit acrylic acid/melamine resin electrophoretically at the film-removed area. The resin deposited on the specimen was finally cured by heating.

It was found that scratching with the AFM probe on open circuit leads to the contamination of the probe with resin, due to positive shifts in the potential during scratching. Scratching of the specimen under potentiostatic conditions at −1.0 V, however, resulted in successful resin deposition at the film-removed area without probe contamination. The rate of resin deposition increased as the specimen potential becomes more positive during electrophoretic deposition. Arrays of resin dots with a few to several tens μm diameter and 100–1000 nm height, and resin walls with 100–1000 nm height and 1 μm width were obtained on specimens by successive anodizing, probe processing, and electrophoretic deposition.

Fabrication of Cu micro-pattern on organic resin board by electroless plating and laser irradiation

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J. Surf. Fin. Soc. Jpn., **59**, 555-561 (2008)

A printed circuit board with a fine Cu pattern was fabricated by electroless plating and laser irradiation. A glass fiber-reinforced epoxy resin plate was immersed in a Pd^{2+} solution and a Cu layer was then deposited on the epoxy resin by Cu electroless plating. After Cu plating, the Cu deposited specimen was irradiated with a pulsed Nd-YAG laser through an iris diaphragm and a convex lens to remove the Cu layer locally in air or doubly distilled water. The width of the Cu removed area increased with increasing the laser power and with decreasing the scanning rate of the laser beam. When laser irradiation was performed in doubly distilled water, the Cu layer around the laser-irradiated area rolled up, resulting in the formation of less precise patterns. Fine Cu-pattern coils with 60 μm width and 20 μm intervals were fabricated on the epoxy resin by laser irradiation in air. (in Japanese)

Thick Platinum layer deposition on ceramics by electroless- and electro-plating

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J. Surf. Fin. Soc. Jpn., **59**, 51-56 (2008)

A thick platinum metal layer was deposited on ceramics using electroless- and electro-plating. The ceramics, which consist of ZrO_2, Al_2O_3, SiO_2, Na_2O, and other oxides, were etched in HF solution, and then immersed in a platinum electroless plating solution containing $Pt(NH_3)_2(NO_2)_2$ and N_2H_4 as a reducing regent. The mass of the ceramics specimen decreased slightly with the electroless plating time and then increased at a rate depending on temperature, but independent of Pt^{2+} concentration. A 2μm thick platinum layer could be deposited uniformly on ceramics by electroless plating for 14.4ks at 323K. Electroplating of platinum in $Pt(NH_3)_2(NO_2)_2$ solution after electroless plating caused the formation of a platinum layer as think as several tens of microns, and many cracks were formed on the platinum layer after a long period of electroplating. (in Japanese)

Corrosion behavior of Al and Al alloys in dilute chloride ion containing solutions

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Proc. of Eurocorro2008, 2185 (2008)

Aluminum and its alloys are widely used because of their high strength-weight ratio and good corrosion resistance. The corrosion rate of such materials mainly depends on the concentration of chloride ions in the environment. However, aluminum and its alloys are sometimes corroded even in tap or fresh water environments. The corrosion behavior of aluminum and commonly used aluminum alloys were investigated by immersion corrosion tests in dilute chloride ion containing solutions, as well as in tap water and bottled water. The electrochemical behavior of highly pure aluminum in the solutions was also investigated. The corrosion products were found after long time immersion tests in all examined solutions and alloys. The 3003-H24 alloy showed relatively low corrosion resistance in tap water and in the artificial tap water investigated here. The pitting potential increased exponentially with decreasing concentration of chloride ions. In solution with chloride ion concentration was lower than 1 mol/m^3, pitting corrosion did not occur on aluminum up to 10 V, because of anodic oxide film formation in dilute chloride ion containing solutions.

Metallic micropatterns on anodic alumina: laser-assisted exposure of trapped seeds for metallization

H. Jha, T. Kikuchi, M. Sakairi and H. Takahashi

ECS Transactions, **11**, 133-141 (2008)

A simple and effective method for the synthesis of aluminum oxy-hydroxide nanofiber is demonstrated. In this method, porous anodic oxide film of aluminum (porous anodic alumina) is used to synthesize the nanofibers, where it acts both as a precursor as well as the template. Initially, the porous oxide film is hydrothermally treated for the formation of hydroxide (boehmite or pseudoboehmite) inside the oxide pores, and then the porous oxide is selectively etched from the film, using tri-sodium citrate solution, leaving the hydroxide intact. The method results in highly uniform aluminum oxy-hydroxide nanofibers. The size (diameter) of the nanofiber was controlled by controlling the size of the pores in the anodic oxide film.

Three-Dimensional Micro-Actuator Fabrication by Aluminum Anodizing, Laser Irradiation, and Electrodepopsition

T. Kikuchi, S. Ueda, Y. Akiyama, M. Ueda, M. Sakairi and H. Takahashi

ECS Transactions, **11**, 29-35 (2008)

Three-dimensional micro-actuators, consisting of three-layer structure of acrylic acid resin / Au / polypyrrole, were fabricated by aluminum anodizing, laser irradiation, and electrochemical techniques. Anodized aluminum tube specimens were irradiated with a pulsed Nd-YAG laser to remove anodic oxide films, and then an Au layer was deposited at the area where film had been removed. The subsequent electrophoretic deposition of acrylic acid resin on the Au layer, dissolution of anodic oxide film and the metal substrate, and deposition of polypyrrole on backside of Au layer by electro-polymerization enabled the fabrication of a three-layer actuator. Cyclic voltammetry of the actuator showed that redox reactions of polypyrrole are accompanied with doping and dedoping of hydrated cations. The three-dimensional micro-actuator showed good performance as a manipulator, gripping and moving objects of several mg in solutions.