ANNUAL REPORT

2009

CORROSION RESEARCH
Materials Science and Engineering

Published
by
THE CORROSION RESEARCH GROUP
HOKKAIDO UNIVERSITY

No. 38

For additional copies and more information, please write to the group members

Prof. T. Ohtsuka: CORROSION ENGINEERING LABORATORY
Prof. H. Habazaki: INTERFACIAL ELECTROCHEMISTRY LABORATORY
Prof. K. Kurokawa: LABORATORY OF HIGH TEMPERATURE MATERIALS
Prof. S. Ukai: LABORATORY OF ADVANCED HIGH-TEMPERATURE MATERIALS
Prof. T. Yonezawa: LABORATORY OF INTERFACE OF MATERIALS AND SURFACE
Prof. T. Narita: ADVANCED COATING LABORATORY
Prof. K. Azumi:
Prof. R. O. Suzuki:
Assoc. Prof. K. Fushimi:

Faculty of Engineering, Hokkaido University
Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan

Prof. F. Watari: BIOMEDICAL, DENTAL MATERIALS AND ENGINEERING LABORATORY

Graduate School of Dental Medicine, Hokkaido University
Kita13, Nishi7, Kita-ku, Sapporo 060-8586, Japan

CONTENTS

Page

CURRENT ACTIVITIES and PRESENTATIONS

AFFILIATE MEMBERS

ABSTRACTS of PUBLICATIONS

CURRENT ACTIVITIES and PRESENTATIONS

CORROSION ENGINEERING LABORATORY

Prof. Dr. Toshiaki Ohtsuka
TEL/FAX: +81-11-706-6351
E-mail: ohtsuka@eng.hokudai.ac.jp
Assoc. Prof. Dr. Mikito Ueda
TEL / FAX: +81-11-706-7813
E mail: mikito@eng.hokudai.ac.jp
Ms. Masako Ogura
TEL/FAX: +81-11-706-6351
E-mail: masako@eng.hokudai.ac.jp

Students

Nan Sheng, Resabal Vannie Joy, S. Kaneko, Y. Tabei, S. Tanaka, K. Nishimoto,
Y. Numata, Y. Sugawara, K. Yamanaka, K. Wakai, S. Hariyama, K. Honda,
H. Matsunaga, M. Koya, W. Murakami

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 molybdo-phosphate (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 steel sheet can be passivated by oxidative property of the PPy and MoP ions doped in PPy layer. The passivation is maintained for more than one month in 3.5 % NaCl aqueous solution. The self-healing property of the coated steel was also examined. When a small failure is inserted on the PPy coated steel, the potential initially falls down and, however, it recovered to the passive region in a few hours. It is observed that the failure site is covered by the molybdate layer which is assigned by micro-Raman spectroscopy.

(2) In-situ monitoring of corrosion products on zinc alloy coated steels by Raman spectroscopy

Transient of corrosion products on zinc and zinc-aluminum alloy layer covering steel in atmosphere were studied during exposure in humidified atmosphere for 3 days by Raman spectroscopy under the in-situ and ex-situ condition. In the presence of NaCl precipitate, the initial product of ZnO changes to zinc-hydroxy carbonate and zinc-hydroxy chloride were detected followed by the aqueous $ZnCl_2$ surface layer which is formed by absorption of water from the humidified air and by corrosion of Zn. The ratio of the amount between zinc-hydroxy carbonate and zinc-hydroxy chloride depends on the amount of NaCl precipitate. The addition of aluminum to the coating requires long time periods before the zinc-hydroxide compounds appear and much decreases the amount of the corrosion product.

(3) Pt monolayer on Pd for application of PEFC cathode

As the cathode of PEFC with high performance for the oxygen reduction reaction (ORR), Pt electrode can be used and for decrease of the amount of Pt, surface coating of Pt on the less expensive metals has been proposed. Pt monolayer coating on Pd single crystals was prepared as a model electrode for ORR as the following way. Initially the Pd single crystal is covered by under-potential-deposition (UPD) of Cu in $CuSO_4$ solution and then the Cu UPD layer is replaced with Pt in K_2PtCl_4 solution. The current for ORR measured in 0.05 M H_2SO_4 is compared between the electrodes of the Pd bulk, Pd-Pt alloy, Pd single crystal covered by Pt monolayer, and Pt bulk. The small efficiency of Pd electrode for ORR is much improved by the coating of Pt monolayer.

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

Al-Zn-X(X=Mo, Mn) alloys were electrodeposited in $AlCl_3$-NaCl-KCl molten salt containing $ZnCl_2$ and $MoCl_3$ 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 Mo content increases from 0 to 3 at% at the same potential region. The surface morphology of the deposit was flat and, however, some cracks exist in the deposit surface.

(5) 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 in hydrogen atmosphere, Tl ion changed to metallic Tl and then the glass exhibited strong light absorption in visible light from 400 to 700 nm wavelength.

(6) Corrosion product of Mg alloys during exposure in humid air

The corrosion products were assigned by Raman spectroscopy and IR spectroscopy. For the IR measurement, KBr pellet technique and reflection absorption technique were used. The standard spectra of various magnesium compounds were measured for this spectroscopy.

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

The Na-S battery developed since a decade years and now will be widely used for energy storage. The development of a new electro-refining process of metallic sodium form the used Na-S batteries may be required. We investigated various non-aqueous electrolytic melts for the process and found that propylene carbonate was suitable for the electrolytic melt in the process. In the electrorefining experiment in propylene carbonate, 99.9% pure metallic sodium was yielded from simulated mixture of the used Na-S battery.

(8) Property of Rust Layer on Weathering Steels

Rusts were formed on weathering steel exposed in humidified air with precipitate of Na_2SO_4 and NaCl at various amounts. The composition of the rust was determined by Raman spectroscopy under in-situ and ex-situ condition. When the rust was formed in the Na_2SO_4 precipitate at large amount on the steel, α-FeOOH covered the whole surface of the steel, and at small amount, it covered the surface by patch-like and Fe_3O_4 and γ-FeOOH covered the other part. When the rust was formed in the NaCl precipitate at large amount, β-FeOOH was found and at small amount, β-FeOOH, Fe_3O_4, and γ-FeOOH were formed. When one pursuits the change of the corrosion product under in-situ condition in the presence of NaCl precipitate at large amount, initially γ-FeOOH was seen, then β-FeOOH increased, and after 2-3 days, γ-FeOOH again increased. When β-FeOOH is formed, free Cl^- is fixed in β-FeOOH and thus the decrease of Cl^- concentration in the surface aqueous layer formed from the humidified air after the long exposure may induce the secondary formation of γ-FeOOH. The properties of the rusts formed by various conditions were also examined by Near IR reflection spectroscopy and AC impedance spectroscopy as well as the amount of water absorbed.

(9) Corrosion Behavior of Longline Fishing Hooks Coated by Green Solders Free from Lead

The present fishing hooks are covered by tin-lead solder for enough protection against corrosion in marine environment. The use of lead may be inhibited in future and thus the replacement coating may be required. The corrosion and adhesion of tin-silver alloys were investigated. The tin-silver alloys coating on the steel hook reveals anti-corrosivity in artificial seawater and in costal environment comparable to the ordinary tin-lead alloy.

Other Activities

Prof. Ohtsuka attended the Asia Steel 2009 held in Pusan/ Korea on May 24-27, 2009 and presented a paper of “Protective Properties of Rust Layers on Weathering Steel”. He attended International Conf. on Materials Engineering for Resources (ICMR) 2009 Akita held in Akita/ Japan on October 21-23, 20 and presented a paper of “Passive oxide films and their in-situ detection”.

Assoc Prof. Ueda attended the ECS annual meeting, Vienna, Austria, Oct.4-9, 2009, and presented a paper entitled by “Na electrodeposition in propylene carbonate containing $NaPF_6$”.

Presentations

Photoluminescence from anodic oxide film of SUS304 in acidic or neutral solution,

Y. Mito, M. Ueda and T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Muroran, January 22-23, 2009

Deposition potential of sodium in propylene carbonate containing $NaPF_6$, H. Hayashi, M. Ueda, T. Ohtsuka, Winter Meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Muroran, January 22-23, 2009

Electrodeposition of Al-Mn-Zn alloy in $AlCl_3$-NaCl-KCl molten salt containing $MnCl_2$,$ZnCl_2$, S. Kaneko, M. Ueda, T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, February 2-3, 2009

Investigation of thickness of ion-exchange layer and immersion duration of glass in molten salt, Y. Aoyama, M. Ueda, T. Ohtsuka, The Joint Meeting of The Hokkaido Sections of ECS Jpn, Surf. Finish. Soc. Jpn. and Jpn. Soc. Corros. Eng., Sapporo, February 2-3, 2009

Ramman spectroscopy of initial rust in weathering steel, S. Tanaka, M. Ueda, and T. Ohtsuka, The 3rd. student symposium on Hokkaido branch of Spectroscopic Society of Japan, Sapporo, March 16, 2009

Continuous measurement of corrosion products on Zn-Al alloy plating layer, A. Saito, M. Ueda and T. Ohtsuka, The 3rd. student symposium on Hokkaido branch of Spectroscopic Society of Japan, Sapporo, March 16, 2009

Electroplating of Al-Mn-Zn alloy in $AlCl_3$-NaCl-KCl molten salt containing $MnCl_2$ and $ZnCl_2$, S. Kaneko, M. Ueda and T. Ohtsuka, The 119th Meeting of The Surface Finishing Society of Japan, University of Yamanashi, Kofu, March 16-18, 2009

Electroplating of Al on Mg alloy in ionic liquid, Y. Tabei, M. Ueda and T. Ohtsuka, The 119th Meeting of The Surface Finishing Society of Japan, Kofu, March 16-18, 2009

Transient change of corrosion products on zinc alloy surface finishing steel - in-situ measurement of Raman scattering spectroscopy, T. Ohtsuka, The 157th Spring meeting of ISIJ, Tokyo, March 28-30, 2009

Na electrodeposition in propylene carbonate containing $NaPF_6$ and morphology of the electrodeposit, M. Ueda, H. Hayashi and T. Ohtsuka, The 144th Spring meeting of the Japan institute of metals, Tokyo, March 28-30, 2009

Electroplating of Al-Mn-Zn alloy in chloride molten salt containing $MnCl_2$ and $ZnCl_2$, M. Ueda, S. Kaneko and T. Ohtsuka, The 76th meeting of Electrochemical Society of Jpn., Kyoto, March 29-31 2009

Corrosion resistance and dissolution of PdCo and PtCo alloys as a PEFC cathode, Y. Tamura, M. Ueda and T.Ohtsuka, Zairyo-to-Kankyo 2009, Tokyo, May 22-24, 2009

Effect of Nickel Addition to Steels on the Rust Formed During 1-3 Years Exposure to Atmosphere, Vannie Joy T. Resabal and T. Ohtsuka, Zairyo-to-Kankyo 2009, Tokyo, May 22-24, 2009

Protective Properties of Rust Layers on Weathering Steel, T. Ohtsuka, V. J. T. Resabal, H. Iwasaki, and S. Tanaka, Asia Steel 2009, No. S9-22, Pusan/ Korea, 24-27 May, 2009

Corrosion protection of steel covered by conductive polypyrrole film containing molybdo-phosphate ion, K. Nishimoto, M. Ueda and T. Ohtsuka, Annual Meeting 2009 of Hokkaido branch of The Chemical Society of Japan, Tomakomai, July 11, 2009

Characterization of the rust layer formed on the nickel containing steels, Vannie. J. T. Resabal, S. Tanaka and T. Ohtsuka, A meeting 2009 of Hokkaido branch of The Chemical Society of Japan, Tomakomai, July 11, 2009

Raman spectroscopy of initial rust of weathering steel under the dry and wet condition, S. Tanaka and T.Ohtsuka, Fall Meeting of ECSJ 2009, Tokyo, September 10-11, 2009

Development of electrorefining process of Na from used Na-S secondary battery, M. Ueda, Fall Meeting of ECSJ 2009, September 10-11, 2009

Passivation and corrosion protection of steel plate covered by conductive polypyrrole bi-layer, K. Nishimoto and T. Ohtsuka, The 145th Fall meeting of the Japan institute of metals, Kyoto, September 15-17, 2009

Corrosion protection of steels by conductive polypyrrole film, T. Ohtsuka, The 158th Fall meeting of ISIJ, Kyoto, September 15-17, 2009

In-situ continuous measurement of corrosion products on galvanized steel, A. Saito and T. Ohtsuka, The 158th Fall meeting of ISIJ, Kyoto, September 15-17, 2009

Effect of electroplating temperature for Al plating on Mg alloys in EMIC-$AlCl_3$ melt, Y. Tabei, M. Ueda and T. Ohtsuka, The 120th Meeting of The Surface Finishing Society of Japan, Chiba, September 17-18, 2009

Characteristics of cathodic electrodeposition in $AlCl_3$-NaCl-KCl molten salt containing $MoCl_3$-$ZnCl_2$, S. Kaneko, M. Ueda and T. Ohtsuka, The 120th Meeting of The Surface Finishing Society of Japan, Chiba, September 17-18, 2009

Na electrodeposition in propylene carbonate containing $NaPF_6$, M. Ueda, ECS 216th meeting of ECS, Vienna Austria, October 4-9, 2009

Techniques for prolonging the life time of metals, T. Ohtsuka, Special public lectures of Hokkaido University, Sapporo, October 17, 2009

Passive oxide films and their in-situ detection, T. Ohtsuka, International Conf. on Materials Engineering for Resources (ICMR) 2009 Akita, p. 2009, Akita, October 21-23 2009

Electroplating of Al-Mn-Zn alloy on mild steel in $AlCl_3$-NaCl-KCl, S. Kaneko, M. Ueda and T. Ohtsuka, The 41th meeting of Molten Salt Chemistry and Technology, Kyoto, November 19-20, 2009

Electroplating of Al on Mg-Al alloys in EMIC-$AlCl_3$ ionic liquid, Y. Tabei, M. Ueda and T. Ohtsuka, The 41th meeting of Molten Salt Chemistry and Technology, Kyoto, November 19-20, 2009

Corrosion protection of steels covered by conductive polypyrrole bi-layer film, T. Nishimoto, M. Ueda, T. Ohtsuka, Corrosion Dream 2009, The committee of corrosion science in Electrochemical Society Japan, Sapporo, December 4, 2009

Recycle of used sodium-sulfur battery, M. Ueda, Eco Products 2009, Tokyo, December 10-12, 2009

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: Bunko Keiki, single type of spectrometer equipped with 532 nm solid laser, cut-edge filter, and high sensitive CCD.
FT-IR Spectrometer: JASCO FT/IR 4200 equipped with MCT detector, IR-RAS apparatus, and IR microscopy system.
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.
ICP atomic emission spectrometer: Thermo i-CAP 6000.
Electrochemistry apparatuses.
Optical Microscopy
Electrochemical Corrosion Rate Monitor System.
Molten salt ion-exchange apparatus for glass.

INTERFACIAL ELECTROCHEMISTRY LABORATORY

Prof. Dr. Hiroki Habazaki
TEL./FAX: +81-11-706-6575
E-mail: habazaki@eng.hokudai.ac.jp
Assoc. Prof. Dr. Yoshitaka Aoki
TEL./FAX: +81-11-706-6752
E-mail: y-aoki@eng.hokudai.ac.jp

Visiting Professor

Prof. Emeritus Dr. Masahiro Seo
TEL./FAX: +81-11-706-6735
E-mail: masaseo@eng.hokudai.ac.jp
Prof. Dr. Soo-Gil Park
E-mail: sgpark@chungbuk.ac.kr

Students

M. T. Tanvir, S. Koyama, S. Yang, S. Ono, S.P. Sah, T. Fujii
Y. Fukunaga, S. Komiyama, K. Ogawa, M. Teraoka, A. Harada, Y. Fang
Y. Konno, S. Tsunekawa, T. Misawa

In July, Professor Soo-Gil Park, Dean of Research Center of Energy Storage, Chungbuk National University, Korea joined our group as a visiting professor. Dr Damian Kowalski left our group and he is now working with Professor Patrik Schmuki, University of Erlangen and Numberg. Mr. Muhammad Tauseef Tanvir got a PhD degree in September, and returned to Pakistan.

The research activities of the laboratory are directed to the development of advanced oxide films and nanomaterials utilizing anodic oxidation process and spin casting. 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) Proton-conducting oxide nanofilms

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. We also found a first example of the proton-conducting anodic ZrO_2-WO_3 films.

(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. Unique microcone-shaped nanoporous anodic niobium oxide films are also fabricated by simple anodizing in phosphate-glycerol electrolyte. Superhydrophobicity has been successfully realized using the anodic oxide microcones. Crystallization of the anodic oxide during anodizing is a key to form the microcone oxide films.

(3) 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.

(4) 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. We found two-step spark anodizing improve markedly the adhesion of the coating without degradation of high wear resistance.

(5) 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.

Other Activities

In August, Prof. H. Habazaki visited Harbin Engineering University and presented an invited paper entitled “Template-assisted synthesis of carbon nanofibers and their electrochemical properties” at 1st Collaborative and Cooperative Symposium between Harbin Engineering University and Hokkaido University. He also attended 216th ECS Meeting, Vienna, Austria in October, and presented a paper entitled “Efficient Proton Conduction in Anodic ZrO_2-WO_3 Films”. He was also invited 12th Joint Symposium between Soul National University and Hokkaido University held in Soul, Korea and 9th International

Symposium on Nanotech. Materials for Next Generation Green Energy System held at Chungbuk National University in Korea in November.

Presentation

M. Seo, K. Fushimi, H. Habazaki, T. Nakayama, “Polarization Behavior of Nickel in Acidic Perchlorate and Acetate Buffer Solutions Containing Small Amount of Pb^{2+}”, 60th ISE Annual Meeting, 16-21 August, Beijing, China (2009).

S. Koyama, Y. Aoki, H. Habazaki, “Interrelationship between structure and composition of anodic oxide films formed on Zr-Si alloys”, 60th ISE Annual Meeting, 16-21 August, Beijing, China (2009).

S. Yang. Y. Aoki, H. Habazaki, “Formation of porous anodic alumina in hot phosphate-glycerol electrolyte”, 60th ISE Annual Meeting, 16-21 August, Beijing, China (2009).

D. Kowalski, Y. Aoki, H. Habazaki, “Proton conductivity in amorphous anodic oxide films of ZrO_2-WO_3”, 60th ISE Annual Meeting, 16-21 August, Beijing, China (2009).

H. Habazaki, Template-assisted synthesis of carbon nanofibers and their electrochemical properties, 1st Collaborative and Cooperative Symposium between Harbin Engineering University and Hokkaido University, 10-11 August, Harbin Engineering University, Haribin (2009).

M. T. Tanvir, Y. Aoki, H. Habazaki, “Electric properties of anodic oxide films formed on porous Ti-Si single phase alloy”, The 3rd GCOE Int. Symp. on Catalysis as the Basis for the Innovation in Materials Science –Beyond the Horizon of Materials Chemistry -, 14-15 September, Hokkaido Univ., Sapporo (2009).

D. Kowalski, Y. Aoki, H. Habazaki, “Proton conduction in anodic zirconia tungstate nanofilms”, The 3rd GCOE Int. Symp. on Catalysis as the Basis for the Innovation in Materials Science –Beyond the Horizon of Materials Chemistry -, 14-15 September, Hokkaido Univ., Sapporo (2009).

T. Fujii, Y. Aoki, H. Habazaki, “Formation of Al-Nb alloy nanocolumns by oblique angle deposition and their application”, The 3rd GCOE Int. Symp. on Catalysis as the Basis for the Innovation in Materials Science –Beyond the Horizon of Materials Chemistry -, 14-15 September, Hokkaido Univ., Sapporo (2009).

S. Koyama, Y. Aoki, H. Habazaki, “Nanocrystallization and capacitance enhancement of anodic ZrO_2-SiO_2 films”, The 3rd GCOE Int. Symp. on Catalysis as the Basis for the Innovation in Materials Science –Beyond the Horizon of Materials Chemistry -, 14-15 September, Hokkaido Univ., Sapporo (2009).

S. Yang, Y. Aoki, H. Habazaki, “Influence of water content on growth of porous anodic alumina in hot phosphate-glycerol electrolyte”, The 3rd GCOE Int. Symp. on Catalysis as the Basis for the Innovation in Materials Science –Beyond the Horizon of Materials Chemistry -, 14-15 September, Hokkaido Univ., Sapporo (2009).

D. Kowalski, Y. Aoki, H. Habazaki, “Efficient Proton Conduction in Anodic ZrO_2-WO_3 Films”, 216th ECS Meeting, 4-9 October, Vienna (2009).

H. Habazaki, “Anodic oxide films on valve metals for electrochemical energy conversion”, 12th Joint Symp. between Soul National Univ. and Hokkaido Univ., 19 November, Soul National Univ., Soul (2009).

T. Fujii, Y. Aoki, H. Habazaki, “Surface wettability of Al alloy nanocolumnar films prepared by oblique angle sputter deposition”, 12th Joint Symp. between Soul National Univ. and Hokkaido Univ., 19 November, Soul National Univ., Soul (2009).

S. Yang, Y. Aoki, H. Habazaki, “Growth behavior of nanoporous anodic alumina films in hot phosphate-glycerol electrolyte”, 1^{2th} Joint Symp. between Soul National Univ. and Hokkaido Univ., 19 November, Soul National Univ., Soul (2009).

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.

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.

Contact angle meters: Kyowa Interface Science, Dropmaster system, to evaluate superhydrophobicity of solid surface.

Q-mass: Balzers Quadstar421 system for mass analysis of gases with mass number of less than 200.

LABORATORY OF HIGH TEMPERATURE MATERIALS

Prof. Dr. K. Kurokawa
Tel+81-11-706-7572, Fax+811-11-706-7119
E-mail: kurokawa@eng.hokudai.ac.jp
Assi. Prof. Dr. A. Yamauchi
Tel+81-11-706-6818, Fax+811-11-706-7119
E-mail: akira-y@eng.hokudai.ac.jp
Visiting Prof. Dr. S. Taniguchi
Tel+81-11-706-7196, Fax+811-11-706-7119
E-mail : s-tanigu@eng.hokudai.ac.jp

Foreign Researcher

Dr. A. K. Nanda Kumar

Students

T. Ito, T. Kurosaki, T. Shoji, H. Takaki, T. Sudiro, T. Sano, T. Kawamoto,
S. Kirai, H. Nakata, T. Inoue, K. Kimura, Y. Fujimoto, T. Yokata

Technical Staffs

Ms. M. Ogura, Ms. E. Ogawa

Research work at “Laboratory of high temperature materials” directs toward 1) high-temperature corrosion of Cr-Si-Ni and CoNiCrAlY alloys, 2) microstructures of oxidation scales formed on NiAl-X alloys, 3) structures of oxide scales formed on carbon steels, stainless steels and aluminum alloys in H_2O-containing atmospheres, 4) scale failure characteristics using acoustic emission (AE), 5) Sintering and oxidation behavior of nano WC, 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 and CoNiCrAlY alloys

High-temperature corrosion tests of Cr-Si-Ni and CoNiCrAlY alloys have been examined. Cr added CoNiCrAlY alloys have poor corrosion resistance to molten Na_2SO_4 and NaCl salts, compared with CoNiCrAlY alloys. On the other hand, 30mass%Si added CoNiCrAlY alloy has an excellent corrosion resistance to molten Na_2SO_4 and NaCl salts. These results suggest that addition of 30mass% Si has a good effect on the corrosion resistance of CoNiCrAlY alloy, but the addition of Cr adversely leads to lowering the corrosion resistance of CoNiCrAlY alloys.

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

In order to clarify the microstructures of oxide scales formed on NiAl-X (X=Mo, Nb) alloys, the oxidation tests in air have been done. Microstructures of oxide scales formed on NiAl-X alloys are observed by FE-SEM and TEM. The addition of Mo to the β-NiAl suppresses the scale growth and formation of interfacial voids, and improves the adhesion of scale compared with NiAl without additional elements. It is supposed that the addition of Mo improves the scale adhesion due to the promotion of transformation of Al_2O_3 from θ or γ to α. On the other hand, the addition of Nb to the β-NiAl promotes the scale growth and scale failure. It is suggested that the addition of Nb promotes the growth of the oxide scale due to the enhancement of outward Al ion diffusion.

(3) 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 Mo added ferritic stainless steels, oxidation tests are being done in H_2O-containing atmospheres. In the ferritic stainless steel without Mo, it is observed that the Cr_2O_3 scale has large cracks. On the other hand, in the Mo added ferritic stainless steel, we found a decrease in the number and length of cracks in the Cr_2O_3 scale. From the result of TEM-EDS analysis, it is confirmed that the Cr_2O_3 scale contains a little bit of Mo. These results suggest that Mo improves the property of Cr_2O_3 scale and suppresses the deterioration of scale failure. Similarly, oxidation behavior and scale structures of carbon steels and Al-Mg alloys in H_2O-containing atmospheres are also being investigated.

(4) Scale failure characteristics using acoustic emission (AE)

In order to clarify the scale failure characteristics, we have done acoustic emission (AE) measurements during isothermal oxidation tests and cooling. The results showed that the presence of water vapor and the increase in Si content in the carbon steel tend to promote the scale failure. Moreover, we investigated the influence of cooling rates on the scale failure. Failure characteristics of scales are attributable to the cooling rate, scale structure, and eutectoid reaction. In general, higher cooling rate leads to higher strain rate and there may be a temperature gradient across the scale thickness, which would additionally enhance the scale failure.

(5) Sintering and oxidation behavior of nano WC

To clarify the mechanisms behind the microstructural evolution during sintering of ultra fine WC and WC-SiC, sintering was interrupted at various temperatures and the kinetics of grain growth was analyzed. The observations suggest that there is a preferential wetting of the WC grains by the liquid phase (Si) responsible for the coarsening process. The observed relation between the grain size and stroke change rate is explained on the basis of the rate equations for densification and coarsening.

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

The corrosion behavior of low carbon steel-X (X=Cr, Ti and Mo) alloys in molten Sn-3.0mass%Ag -0.5mass%Cu solders have been investigated. A $FeSn_2$ layer is formed in all the specimens in the interfacial reaction at 623 to 723 K. The addition of Cr or Ti to the low carbon steel improves the thickness of consumed substrate due to suppression of interfacial reaction than those without Cr and Ti. On the other hand, the addition of Mo to carbon steel does not improve the resistance against interfacial reaction because of the formation of Mo rich ferrite phase which is corroded easily. These results indicate that the microstructure of metal substrate has influence on the interfacial reaction. The thickness loss of carbon steel with Cr follows a parabolic law.

Other Activities

In August, Prof. Kurokawa attended the International Symposium on Applied Plasma Science 2009 held in Hamburg, Germany, and presented papers entitled “The Influence of Cr Addition on the High Temperature Corrosion of CoNiCrAlY Alloys”.

Presentations

Influence of oxidation temperature on morphology of oxide scale formed on Al-Mg alloys; A. Yamauchi, T. Kurosaki, R. Tu, T. Goto and K. Kurokawa: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Muroran, Jan., 2009.

Reaction behavior of commercial steels in molten lead-free solders; A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: Mate2009, Yokohama, Jan., 2009.

Formation of microstructures of Sn-based alloys at minute stress loading; H. Takagi, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: ibid.

Variation of cooling rate on cast structure of multi Sn-Ag alloy systems; S. Kirai, A. Yamauchi, K. Kurokawa and J. Tanaka: 2009 Winter Joint Meeting Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem., Sapporo, Feb., 2009.

Effect of additional element on interfacial growth between Fe-based alloys and molten lead-free solder; T. Kawamoto, A. Yamauchi, K. Kurokawa and J. Tanaka: ibid.

Formation mechanism of sub-grain structures of lead-free solders; H. Takagi, A. Yamauchi, K. Kurokawa and J. Tanaka: ibid.

Influence of oxidation temperature on oxide scale formed on Al-Mg alloys; A. Yamauchi, T. Kurosaki, R. Tu, T. Goto S. Taniguchi and K. Kurokawa: The 143rd Annual Meeting of Jpn. Inst. Metals, Tokyo, Mar., 2009.
Effect of additional elements on microstructure of oxide scale formed on β-NiAl; K. Kurokawa, T. Ito, H. Tomoto and A. Yamauchi: ibid.

Optimum Al content of Al reservoir layer in Ni super alloy/ Re-Cr-Ni(-W) σ phase/Al reservoir system; S. Saito, K. Kurokawa, T. Takashima, S. Hayashi and T. Narita: ibid.

Damage behavior of oxide scale formed on Si containing steel -Effect of Si content and water vapor-; H. Nakata, A. Yamauchi, S. Taniguchi and K. Kurokawa: The Summer Join t Meeting of The Hokkaido Secs. of Jpn. Inst Metals and Iron and Steel Inst. Jpn., Muroran, July, 2009.

Influence of molten Na_2SO_4+ NaCl salts on high temperature corrosion behavior of STBA21 and Cr-Si-Ni compacts; T. Sano, T. Sudiro, A. Yamauchi, S. Taniguchi and K. Kurokawa: ibid.

Corrosion behavior of Fe-based alloys in molten lead-free solder; T. Kawamoto, A. Yamauchi, K. Kurokawa and J. Tanaka: ibid.

Effect of composition on microstructure of Sn-Ag solders; S. Kirai, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: The 19th Symposium of Micro Electronics, Fukuoka, Sep., 2009.

Corrosion behavior of Fe-based alloys with additional elements in molten lead-free solders; T. Kawamoto, A. Yamauchi, A. Irisawa, S. Kawakubo, K. Kurokawa and J. Tanaka: ibid.

The Influence of Cr Addition on the High Temperature Corrosion of CoNiCrAlY Alloys; T. Sudiro, T. Sano, A. Yamauchi, S. Taniguchi, A. Kobayashi and K. Kurokawa: 7th International Symposium on Applied Science, Hamburg, Germany, August, 2009.

Microstructure of oxide scale formed on Al-Mg alloys in H_2O-containing atmospheres; T. Kurosaki, A. Yamauchi and K. Kurokawa: The 144th Annual Meeting of Jpn. Inst. Metals, Kyoto, Sep., 2009.

Effect of Mo addition on morphology of Cr_2O_3 scale formed on ferritic stainless steels; T. Shoji, A. Yamauchi, S. Taniguchi, K. Kurokawa, K. Fukuda, S. Ishikawa and T. Ujiro: ibid.

Effect of various additional elements on morphology of oxide scale formed on β-NiAl; T. Ito, A. Yamauchi, S. Taniguchi and K. Kurokawa: ibid.

Effect of Si content on damage behavior of oxide scale formed on low carbon steel; H. Nakata, A. Yamauchi, S. Taniguchi, K. Kurokawa, I. Sohn and J. Choi: ibid.

Effect of additional elements on Solid solution behavior of γ' phase in Ni-Al and Ni-Al-Cr system; S. Saito, K. Kurokawa, T. Takashima, S. Hayashi and T. Narita: ibid.

Oxidation Behavior of Combustion Synthesized β-SiAlON in Air; X Yi, A. Yamauchi, K. Kurokawa and T. Akiyama: ibid.

The influence of Cr addition on the high temperature corrosion of CoNiCrAlY alloys; T. Sudiro, T. Sano, A. Yamauchi, S. Taniguchi and K. Kurokawa: The 56th Jpn. Conf. on Materials and Environments, Osaka, Sep., 2009.

High temperature corrosion behavior of Cr-Si-Ni compacts in molten Na_2SO_4+ NaCl salts; T. Sano, A. Yamauchi, S. Taniguchi and K. Kurokawa: ibid.

Corrosion behavior of steel in molten lead-free solder; A. Yamauchi, J. Tanaka and K. Kurokawa: ibid.

Effect of carbide additions on the grain size and mechanical properties of sintered n-WC; A. K. Nanda Kumar, A. Yamauchi, M. Watabe and K. Kurokawa: The 14th Meeting on Spark Plasma Sintering, Sendai, Nov., 2009.

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

Prof. Dr. F.Watari
Tel&Fax:+81-11-706-4251 E-mail:watari@den.hokudai.ac.jp
Assoc. Prof. Dr. M.Uo
Tel&Fax:+81-11-706-4251 E-mail:uo@den.hokudai.ac.jp
Res. Assoc. Dr. T.Akasaka
Tel&Fax:+81-11-706-4251 E-mail:akasaka@den.hokudai.ac.jp
Res. Assoc. Dr. S.Abe
Tel&Fax:+81-11-706-4251 E-mail:sabe@den.hokudai.ac.jp

Foreign Researchers

Dr. Lu Xiong

Students

M.Matsuoka, E.Hirata, K.Ishikawa, S.Ito, T.Koshikawa, Y.Kawai, N.Iwadera

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).

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. Maany 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 psuedopodium 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 were 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 it's 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, 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 that 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:

Dr. Lu Xiong of Southwest Jiaotong University, China joined to our laboratory on October 2009 as the postdoctoral researcher of the Japan Society for Promotion of Science (JSPS) for the development of nano-structured scaffold for medical and biochemical applications.

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.

Presentations

Bioreactivity of nanotubes and nanoparticles, Fumio Watari, 36th meeting of the fullerene nanotube society, Nagoya, Mar. 2009.

Cell culture on carbon nanotubes, Fumio Watari,, Tsukasa Akasaka, Michiko Terada, Takamitsu Koshikawa, Motohiro Uo, Yoshimasa Kitagawa, 119th meeting of the surface finishing society, Kofu, Mar. 2009.

Bioreactivity of nanoparticles –biointeractive and bioreactive properties, Fumio Watari, Atsuro Yokoyama, Tsukasa Akasaka, Motohiro Uo, Shigeaki Abe, Sachiko Ito, Ikuko Oguchi, Yasutaka Yawaka, 31th meeting of Japanese biomaterials society, Nov. Kyoto, 2009.

Nanomaterials and bioreaction: Invitation to Biomedical, F.Watari, M.Uo, T.Akasaka, S.Abe, O.Iuko: 9th Asian BioCeramics Symposium (ABC2009), Dec, Nagoya, 2009.

Carbon nanotubes/collagen composite for biomedical appricātions, Uo M. Terada M., Akasaka T., Kitagawa Y., Watari F.; First International Conference on Multifunctional, Hybrid and Nanomaterials, Tours, Mar. 2009.

Preparation and properties of dental composite resin cured under near infrared irradiation, Uo M., Kudo E., Okada A., Soga K., Kogo Y.; The 26th International Conference of Photopolymer Science and Technology, Chiba, June, 2009.

Micro XAFS analysis of metallic element containing biological specimens using the polycapillary focusing X-ray optics, Uo M., Asakura K., 14th International Conference on X-ray Absorption Fine Structure（XAFS14）; Camerino, July, 2009.

XAFS analysis of corrosion product of Ni-Ti alloy and stainless steel in soft tissue, Motohiro Uo, Tsukasa Akasaka, Shigeaki Abe, Fumio Watari, 53rd The Japanese Society of Dental Materials and Devices, Tokyo, Apl. 2009

XAFS analysis of the corrosion products of Ni-Ti alloy and stainless steel, Uo Motohiro, Watari Fumio, Asaoka Kenzo, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

Rapid analysis of metallic restorations of metal allergy patients, Motohiro Uo, Fumio Watari, Michiko Terada, Yoshimasa Kitagawa, Akiko Mabuchi, Yasunori Totsuka, 54th meeting of the Japanese society of oral surgery, Sapporo, Oct. 2009.

XAFS analysis of corrosion products of biomedical metals, Motohiro Uo, Kiyotaka Asakura, Kenzo Asaoka, Fumio Watari, 12th meeting of XAFS society, Aomori, Sept. 2009.

Capture of Bacteria with Flexible Carbon Nanotubes, Tsukasa Akasaka, Shigeaki Abe, Motohiro Uo, Fumio Watari, the 53th General Session of the Japanese Society for Dental Materials and Devices, Tokyo, Apr.11-12, 2009

Capture of Bacteria and Bactericidal Effect using Carbon Nanotubes, Tsukasa Akasaka, Shigeaki Abe, Motohiro Uo, Fumio Watari, the 54th General Session of the Japanese Society for Dental Materials and Devices, Kagoshima, Oct.1-2, 2009

Bactericidal Effect of Carbon Nanotubes/agar Composite Irradiated with NIR Light on Streptococcus mutans, Tsukasa Akasaka, Makoto Matsuoka, Takeshi Hashimoto, Fumio Watari, the 3rd International Conference on Science and Technology for Advanced Ceramics, Yokohama, Jun.16-18, 2009

Controlled mineralization using biomimetic macromolecule; Daisuke Hayashi, Shigeaki Abe, Tomoki Ishida, Emi Yamatoya, Tsukasa Akasaka, Motohiro Uo, Fimio Watari, and Tomoya Takada, 21st annual meeting of Society for Organ Substitution and Regenaration Medicine, Sapporo, Jan. 2009

Reaction dynamics following electron capture of chlorofluorocarbon adsorbed on water cluster: A direct density functional theory molecular dynamics study; 2009 winter meetings of Japanese Chemical Society, Hokkaido Division, Shigeaki Abe, Fumio Watari, and Hiroto Tachikawa, Sapporo, Jan. 2009

A direct MD study on graphene-water interaction system; Shigeaki Abe, Yoshinori Nagoya, Fumio Watari, and Hiroto Tachikawa, 5th International Conference on Molecular Electronics and Bioelectronics, Miyazaki, March 2009

An ab initio MO study on the structures and electronic states of hydrogen-bonded O_3-H_2O complexes; Shigeaki Abe, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, and Hiroto Tachikawa, 53rd The Japanese Society of Dental Materials and Devices, Tokyo, Apl. 2009

Observation of administered micro/nano-materials in mice; 52nd annual meeting of Japan Society of Microscopy, Mami Mutoh, Shigeaki Abe, Tsukasa Akasaka, Motohiro Uo, and Fumio Watari, Sendai, May 2009

Reaction dynamics of chlorofluorocarbon on ice: A dynamics DFT study; Shigeaki Abe, Fumio Watari, and Hiroto Tachikawa, 22nd symposium on chemical kinetics and dynamics, Omiya, Jun. 2009

Synthesis and charactarization of polyanionic macromolecules with zinc coordinated compound and its application for controlled calcification; Daisuke Hayashi, Shigeaki Abe, Tomoki Ishida, Emi Yamatoya, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, and Tomoya Takada, International Symposium of Photochemistry and Photophysics of Coordinate Compounds, Sapporo July 2009

A DFT and MD study on the interaction of nanocarbon materials with water molecules; Shigeaki Abe, Yoshinori Nagoya, Fumio Watari, and Hiroto Tachikawa, 4th International Conference on Polymer Batteries and Fuel Cells, Yokohama, Aug. 2009

An ab-initio study on interaction between graphene and water molecules; Shigeaki Abe, Fumio Watari, and Hiroto Tachikawa, 3rd annual meeting of Japan Society for Molecular Science, Nagoya, Sep. 2009

Controlled calcification using biomimetic macromolecules with zinc-imidazole coordinated compound; Shigeaki Abe, Daisuke Hayashi, Emi Yamatoya, Tomoki Ishida, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, and Tomoya Takada, 59th Japan society of coodination chemistry symposium, Nagasaki, Sep. 2009

Synthesis of a carbonic anhydrase analogue and its application for controlled calcification; Emi Yamatoya, Tomoki Ishida, Shigeaki Abe, Ikuko Oguchi, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, Daisuke Hayashi, and Tomoya Takada, Kagoshima, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

Photophysical characterization of cumarin doped poly (lactic acid) micro particles and its fabrication for bioimaging; Shigeaki Abe, Iosif D. Rosca, Takayuki Kiba, Kiyotada Hosokawa, Hirohisa Kobayashi, Satoru Nitobe, Takashi Hirota, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki, Shin-Ichiro Sato, and Fumio Watari, 11th International Conference on Electronic Spectroscopy and Surface, Nara, Oct. 2009

Observation of internal distribution of micro/nano-sized ceramics and metals particles in mice; Shigeaki Abe, Nobuki Iwadera, Mami Mutoh, Chika Koyama, Mitsue Esaki, Tsukasa Akasaka, Motohiro Uo, Manabu Morita,Yoshinori Kuboki, Koichi Haneda, Yasutaka Yawaka, Fumio Uchida, Tetsu Yonezawa, and Fumio Watari, 22nd International Symposium on Ceramics in Medicine (Bioceramics22), Daegu Oct. 2009

Observation of biodistribution of several micro/nano-particles in mice and its visualization; Shigeaki Abe, Nobuki Iwadera, Mami Mutoh, Daisuke Hayashi, Ikuko Oguchi, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, Tomoya Takada, and Tetsu Yonezawa, 30th annual meeting of Japanese Society for Biomaterials, Kyoto, Nov. 2009

Evaporation dinamics of water molecules on nanocarbon materials: A DFT and MD study; Shigeaki Abe, Yoshinori Nagoya, Fumio Watari, and Hiroto Tachikawa, 22nd International symposium of microprocesses and nanotechnology, Sapporo Nov. 2009

Internal distribution of several nano-magnetic particles in mice; Shigeaki Abe, Ikuhiro Kida, M. Esaki, Tsukasa Akasaka, Motohiro Uo, Yoshinori Kuboki, Manabu Morita, Koichi Haneda, Balachandran Jeyadevan, Yoshinori Sato, Kazuyuki Tohji, and Fumio Watari, 9th Asian BioCeramics Symposium (ABC2009), Nagoya, Dec. 2009

Controlled mineralization using biomimetic macromolecule with an active reaction center analogue of Carbonic Anhydrase; Shigeaki Abe, Emi Yamatoya, Tomoki Ishida, Daisuke Hayashi, Ikuko Ohguchi, Tsukasa Akasaka, Motohiro Uo, Fumio Watari, and Tomoya Takada, 6th Singapore International Chemical Conference, Singapore, Dec. 2009

Cell adhesion and proliferation on the inner surface of CNT coated 3D scaffold, E.Hirata, M.Uo, A.Yokoyama, F.Watari, The 53rd General Session of the Japanese Society for Dental Materials and Devicess, Tokyo, April.2009
Bone generation using carbon nanohorns –application for CBR method-,T. Kasai, T. Kanamori, E. Hirata, S. Yamamoto, H. Komatubara, A. Yokoyama, ,118th Scientific Meeting of Japan Prosthodontic Society, Kyoto,June.2009

Cell adhesion mechanism on inner surface of multi-walled carbon nanotube coated3D scaffold, E. Hirata, M. Uo, A. Yokoyama, F. Watari, 1st Annual Meeting of the Nano Biomedical Society, Sapporo, July.2009

Development of a 3D Collagen Scaffold Coated With Multiwalled Carbon Nanotubes, E. Hirata, K. Nodasaka, Y. Takita, N. Ushijima, M. Uo, A. Yokoyama, F. Watari, 31_{st} annual meeting of the Japanese Society for Biomaterials, Kyoto, November.2009

Strong Adhesion of Saos-2 Cells to Multi-walled Carbon Nanotubes, M. Matsuoka, T. Akasaka, Y. Totsuka, F. Watari, The Third International Conference on the Science and Technology for Advanced Ceramics (STAC-3), Yokohama, Jun. 16–18, 2009

The development of reconstruction materials having both high cellular adhesiveness and electric conductivity, M. Matsuoka, T. Akasaka, Y. Totsuka, F. Watari, The 54th Congress of the Japanese society of Oral and Maxillofacial surgeons, Sapporo, Oct. 10–12, 2009

The effect of CNT on the growth of hepatic cells, Sachiko Itoh, Tsukasa Akasaka, Yasutaka Yawaka, Fumio Watari; 53rd The Japanese Society of Dental Materials and Devices, Tokyo, Apl. 2009

Development of scaffolds for cell culture using an almino-silicate nanotubes, imogolite, Ishikawa Kosuke, Akasaka Tsukasa, Abe Shigeaki, Uo Motohiro, Watari Fumio, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

The behavior of hepatic cells to carbon nanotubes, Ito Sachiko, Akasaka Tsukasa, Yawaka Yasutaka, Watari Fumio, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

Comparison of osteoblastic responses to aluminosilicate nanotubesm imogolite, K.Ishikawa, T.Akasaka, N.Iwadera, S.Abe, M.Uo, M.Kaga, Y.Yawaka, M.Suzuki, F.Watari; 9th Asian BioCeramics Symposium (ABC2009), Dec, Nagoya, 2009.

Successive observation of phagocytosis-like activity of liver cells for carbon nanotubes, S.Itoh, T.Taira, Y.Yawaka, F.Watari; 9th Asian BioCeramics Symposium (ABC2009), Dec, Nagoya, 2009.

Microsturucture evaluation of the interface between dental zirconia ceramics and porcelain, Y. Kawai, M. Uo, F. Watari i; 53rd The Japanese Society of Dental Materials and Devices, Tokyo, Apl. 2009

Application of flake shaped glass filler containing polycarbonate for non-clasp partial denture, A. Sasaki, M. Uo, K. Iwasaki, S. Abe, T. Akasaka, F. Watari, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

Apatite-like compownd formation on the carbon nanotube surface in body simulated fluid, Takamitsu Koshikawa, Motohiro Uo, Tsukasa Akasaka, Yoshinori Kuboki, Fumio Watari; 53rd The Japanese Society of Dental Materials and Devices, Tokyo, Apl. 2009

Apatite-like precipitation upon carbon nanotubes with calcifying solutions under various conditions, Koshikawa Takamitsu, Kuboki Yoshinori, Abe Shigeaki, Akasaka Tsukasa, Uo Motohiro, Watari Fumio, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

Culture of osteoblast cells and marrow cells on carbon nanotube scaffold, Kitahara Hiromi, Kuboki Yosinori, Akasaka Tsukasa, Watari Fumio, Inoue Nobuo, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

Preparation and properties of thermoplastic resin based nanocomposites for the development of FRP orthodontic wires, Yamagata Shuichi, Akasaka Tsukasa, Uo Motohiro, Iida Junichiro, Watari Fumio, 54th The Japanese Society of Dental Materials and Devices, Oct. 2009

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

Prof. Dr. S. Ukai
Tel./Fax.: +81-11-706-6355
E-mail:s-ukai@eng.hokudai.ac.jp
Assoc. Prof. Dr. S. Hayashi
Tel.:+81-11-706-6357 Fax.:+81-11-706-7814
E-mail:hayashi@eng.hokudai.ac.jp
Tech. Staff Mr. J. Tanaka
Tel./Fax.: +81-11-706-6818

Students

Y. Kitajima, M. Auchi, T. Narita, B. Leng, Q. Tang, S. Takagi, D. Igarashi, M. Yamamoto, A. Minami, T. Matsukawa, S. Kasahara, Y. Sugino, H. Noto, R. Kawano, K. Takezawa, K. Toyota, T. Nii, R. Miyata

The research activities of the laboratory are directed to the development of the advanced high strengthened ODS alloys, and an understanding of the mechanism of the high temperature corrosion, oxidation of metals such as superalloys, inter-metallic compounds, iron-based alloys, and steels.

Current topics on research are in the following:

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

Nano-meso 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 a-g 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 a-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°C. 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°C.

(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 50nm 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-Al based Al_2O_3 forming alloys

The effects of water vapor on the oxidation of γ'-Ni-25at%Al-Pt alloys are still being investigated. Water vapor increased the initial oxidation mass gain on the low Pt containing alloys, but no effect was observed on the exclusive Al_2O_3 forming high Pt containing alloys. For a longer-term oxidation, growth rate of α-Al_2O_3 scale was found to decrease with water vapor present. However it was found that water vapor stabilized metastable Al_2O_3 for a longer time exposure, and the metastable Al_2O_3 grains grew significantly larger with water vapor present.

(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 phase transformation to α-Al_2O_3 scale.

(6) Effect of oxygen content on the stability of an Al_2O_3 scale on Nb(O)-Al-X alloys

The formation behavior of an Al_2O_3 scale on Nb(O)-Al-X alloys are being investigated. Oxygen content in Nb substrate was changed with the addition of Re, Mo, and Ta. The formation behavior of an Al_2O_3 scale on the oxygen saturated Nb(O)-X was conducted by an Al pack-cementation process. A very thin, well adhesive Al_2O_3 scale was found to develop on the alloy with higher oxygen content, but formation of a Nb-aluminide + internal Al_2O_3 mixture layer was observed on the alloy with intermediate oxygen content. Only the Nb-aluminide layers were formed on the alloy with low oxygen content. Using of oxygen as a alloying element for Nb alloys is now under investigating to develop the Nb(O) based Al_2O_3 forming alloys.

(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. This liquid phase was found to penetrate to a FeO scale along the grain boundaries, causing a separation between an oxide scale and a steel substrate. This separation is considered to be one of the reasons of the oxide scale spallation.

(8) Effect of water vapor on the oxidation of pure-Ni

The effect of water vapor on the oxidation of pure-Ni is being investigated. Water vapor was found to have little effect on the oxidation mass change of pure-Ni. However, a duplex oxide layer with outer very porous and inner dense NiO was formed when a pure-Ni was oxidized in an atmospheres containing water vapor. Outer porous layer was found to consist of very fine powder-like NiO, and it was easily detached from the surface. The formation mechanism of the powder-like NiO layer is know under investigating.

Presentations

Phase Transformation Behavior of Al_2O_3 Scale during High Temperature Oxidation: Y. Kitajima, T. Nishimoto, S. Ukai, S. Hayashi and T. Narita: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2009

Mechanism of Recrystallization Textured Microstructure Formation in 12Cr-ODS Ferritic Steels: H. Numata, S. Ukai, S. Hayashi, T. Kaito and S. Ohtsuka: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2009

Nanocrystallization of Nb-base ODS alloy by Mechanical Alloying: A. Minami, S. Ukai and S. Hayashi: The Winter Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan.,2009

Effect of Substrate Elements on the Phase Transformation Behavior of Al_2O_3 Scale at High Temperatures: Y. Kitajima, T. Nishimoto, S. Ukai, S. Hayashi and T. Narita: The Spring Meeting of Jpn. Inst. Metals., Tokyo, Japan, Mar.,2009.

Effect of Water Vapor Atmosphere on High Temperature Oxidation Behavior of Pure Nickel: Y. Kitajima, S. Ukai, S. Hayashi and T. Narita: The Spring Meeting of Jpn. Inst. Metals., Tokyo, Japan, Mar.,2009.

Relationship between Ultrafine Grain Structure and High-Temperature Strength in 9CrODS Ferritic Steels: N. Chikata, S. Ukai, S. Hayashi, T. Kaito and S. Ohtsuka: The Spring Meeting of Jpn. Inst. Metals., Tokyo, Japan, Mar.,2009.

Oxide Particle Evolution and Dispersion Refinement in Ni-base ODS Superalloy by Hf Addition: T. Hoshino, S. Ukai and S. Hayashi: The Spring Meeting of Jpn. Inst. Metals., Tokyo, Japan, Mar.,2009.

Nanocrystallization and Formation of Oxide Particles by Mechanical Alloying in Nb-base ODS alloy: A. Minami, S. Ukai and S. Hayashi: The Spring Meeting of Jpn. Inst. Metals., Tokyo, Japan, Mar.,2009.

$\alpha \rightarrow \gamma$ Phase Transformation in 9CrODS Ferritic Steels: M. Yamamoto, S. Ukai, S. Hayashi, T. Kaito and S. Ohtsuka: The Spring Meeting of Jpn. Inst. Metals., Tokyo, Japan. Mar.,2009.

Formation Behavior of Oxide Particle in Nb-Al System ODS alloy: A. Minami, S. Ukai, S. Hayashi and N. Sakaguchi: The Summer Joint Meeting of Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul.,2009

High-Strength of Modified Ausform 9CrODS Steels: S.Ukai, M. Yamamoto, N. Chikata, S. Hayashi, T. Kaito, S. Ohtsuka, T. Azuma and S. Ohsaki: International Conference on Fusion Reactor Materials, Sapporo, Japan, Sep., 2009.

Reverse Phase Transformation from Ferrite to Austenite in 9CrODS Ferritic Steels: M. Yamamoto, S. Ukai, S. Hayashi, T. Kaito and S. Ohtsuka: International Conference on Fusion Reactor Materials, Sapporo, Japan, Sep., 2009.

Effect of Tungsten Addition on Microstructure and High-Temperature strength of 9CrODSFerritic Steel: T. Narita, S. Ukai, S. Ohtsuka and M. Inoue, International Conference on Fusion Reactor Materials, Sapporo, Japan, Sep., 2009.

Directional Recrystallization of ODS Alloys by Means of Zone Annealing: Y. Sugino, S. Ukai and S. Hayashi: International Conference on Fusion Reactor Materials, Sapporo, Japan, Sep., 2009.

Effect of Fe and Ni Doping on the Phase Transformation of Al_2O_3 Scale: Y. Kitajima, T. Nishimoto, S. Ukai, S. Hayashi and T. Narita: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Short-term Oxidation Behavior of Ni-Al-Pt Ternary Alloy in Atmospheres Containing Water Vapor: M. Auchi, S. Ukai, S. Hayashi and T. Narita: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Effect of Grain Size on High Temperature Oxidation in Fe-Cr Ferritic Steel: D. Igarashi, S. Ukai and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Effect of element additions on High Temperature Oxidation Resistance of Nb-Al alloy: S. Takagi, S. Ukai and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Formation of Oxide Particle in Nb-Al System ODS alloy: A. Minami, S. Ukai, S. Hayashi, N. Sakaguchi and S. Miura: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Relationship between High-Temperature Strength and microstructure of 9CrODS Ferritic Steels: M. Yamamoto, S. Hayashi, S.Ukai, S. Ohtsuka, T. Kaito, T. Azuma and S. Ohsaki: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Effect of Phosphorus and Sulfur on High Temperature Oxidation Behavior of Low-Carbon Steels: S. Kasahara, S. Ukai, S. Hayashi, K. Honda, K. Tanaka and K. Kinoshita: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

Directional recrystallization in Ni-base ODS alloy: Y. Sugino, S. Ukai and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals., Kyoto, Japan, Sep.,2009.

Transient Liquid-Phase (TLP) Bonding of ODS Martensitic Steels: H. Noto, S. Ukai and S. Hayashi: The Autumn Meeting of Jpn. Inst. Metals, Kyoto, Japan, Sep., 2009.

High Temperature Carburization of Hastelloy-X alloy in CH_4 gas: C. Matsukawa, S. Ukai, S. Hayashi and H. Yakuwa: The Autumn Meeting of Jpn. Inst. Metals., Kyoto, Japan, Sep.,2009.

Rapid Phase Transformation to α-Al_2O_3 by Deposition of Various Elements on Al_2O_3-forming Alloys: Shigenari Hayashi, Yuri Kitajima, Takumi Nishimoto, Toshio Narita and Shigeharu Ukai, European Federation of Corrosion Workshop, Frankfurt, Germany, Sep. 2009.

Suppression of metastable Al_2O_3 formation on β-NiAl and FeAl by Various Elements Deposition: Yuri Kitajima, Shigenari Hayashi, Takumi Nishimoto, Toshio Narita and Shigeharu Ukai, Gordon Research Conference, New London, USA, July, 2009.

High Temperature Oxidation Behavior of Ni-Al-Pt Alloys in Atmospheres Containing Water Vapor: M. Auchi, S. Hayashi, T. Narita, S. Ukai, Gordon Research Conference, New London, USA, July, 2009.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 10) Cladding Tube Manufacturing and Summary; S. Ukai, S. Ohnuki, S. Hayashi, T. Kaito, M. Inoue,A. Kimura, T. Fujisawa, T. Okuda, F. Abe, Int. Conf. on Advanced Power Plant, Tokyo, Japan, May, 2009.

LABORATORY OF INTERFACE OF MATERIALS AND SURFACE

Prof. Dr. T. Yonezawa
Tel.:+81-11-706-7110 Fax.:+81-11-706-7881
E-mail:tetsu@eng.hokudai.ac.jp
Assoc. Prof. Dr. M. Sakairi
Tel.:+81-11-706-7111, Fax.:+81-11-706-7881
E-mail: msakairi@ eng.hokudai.ac.jp
Research Associate Dr. T. Kikuchi
Tel.:+81-11-706-7112, Fax.:+81-11-706-7881
E-mail: kiku@ eng.hokudai.ac.jp

Researchers

Dr. H. Jha, Dr. N. Nishida, Dr. A. Hyono, N. Tsukamoto

Technical Staff

M. Sugawara

Secretariat

M. Muarta

Students

Y. Shishino, M. Zheng, K. Kawai, R. Goto. M. Kinjo, K. Yanada, Y. Wachi, J. Tatehara, R. Fujita, S. Fujita, T. Murata, H. Hirano, K. Otani, H. Takahashi, M. Uchida, S. Udagawa, and K. Saito

Prof. T. Yonezawa took his position as the full professor in this laboratory in April 2009. Y. Shishino is a D. Sc. candidate originally belonging to the University of Tokyo and stayed from April 2009 to February 2010 and went back to the University of Tokyo. Drs. N. Nishida and A. Hyono joined our laboratory from April 2009. N. Tsukamoto and M. Sugawara joined to this group as a researcher and a technical staff from January 2010. M. Sugawara quitted this laboratory at the end of March 2010. Dr. N. Nishida quitted this laboratory also at the end of March 2010 and began his academic carrier as a Research Associate of Chuo University (Tokyo). Dr. T. Kikuchi was appointed as an associate professor in this division (Research group of Eco-Process) from April 1, 2010.

The research activities of this group are directed to the development of nanoparticle preparation processes, an understanding of the mechanism of the high temperature corrosion in super alloys, intermetallic compounds and iron-based alloys, and to the development of the corrosion resistant alloys and corrosion protection of steels with a hot dipping method in sea-water front environment. The research activity is also directed to an understanding of the solidification mechanism of metals and Alloys.

Dr. H. Jha left Prof Patrik Schmuki's laboratory in university of Erlangen-Nuremberg Erlangen Germany as postdoctoral researcher on May. 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.

Current topics on research are in the following:

(1) Copper Particle Synthesis and Application

Preparation and application of metallic copper fine and nanoparticles are carried out intensively. From copper oxides (CuO and Cu_2O), non-oxidized metallic copper nanoparticles are successfully prepared by a chemical reduction procedure. Thanks to the optimized covering organic polymer materials, copper particles are not readily oxidized and can be kept in powder form under ambient condition for several months. We are now able to disperse these particles independently and prepare Cu particle pastes. These pastes can be used as a conductive paste.

(2) Liquid plasma to form nanomaterials

Chemical reduction process may be the most common preparative process of nanoparticles, nanorods, as well as nanoplates. However, the preparation solution/dispersion should contain metal source, stabilizers, as well as reducing reagents. Especially stabilizers and reducing reagents are often added large excess amount. On the contrary, energy, such as photo-energy, microwave, sonification are good candidates for chemical reduction energies for nanoparticle preparation. We have recently succeeded to prepare metal nanoparticles by microwave plasma in water. This process is a very rapid and easy process and metal-to-metal preparation is also possible according to very high energy of plasma. 0-valent metal nanoparticles, alloys, metal oxides, as well as composite metal oxides can be prepared by this plasma process.

(3) In-situ observation of nanomaterials in TEM at high temperature

In order to reveal the detailed structural changes of nanosized materials at high temperature were revealed by in-situ TEM observation. With a special gas introducing specimen folder, the sample can be heated up to 1500 °C. With such equipments, we observe the sintering process of copper nanoparticles or other particles, as well as the crystalling process of nanomaterials.

(4) Surface-assisted laser desorption/ionization mass spectroscopy

Mass spectroscopy is one of the most important chemical analyses especially understanding the structure of the unknown compounds. Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy is probably most important MS method in order to understand *m*/*z* values of synthetic polymers as well as biopolymers. This MS method is very easy and UV pulse laser was just irradiated to the mixture of the sample and organic matrix compounds for soft-ionization of the specimens. However, MALDI-MS method is not suitable for the mass analyses of organic molecules in relatively low mass range, *i.e.*, *m*/*z* < 500 because in this mass range, many mass peaks of the fragment ions of the organic matrix itself. The strength of the peaks of such ions is very strong compared to the sample ions. In order to overcome such problems, surface-assisted laser desorption/ionization (SALDI) mass spectroscopy has been intensively studied recently. Our laboratory provides various metal and inorganic nanoparticles for that purpose.

(5) Corrosion of Al alloy in model tap water

An influence of K^+ and Na^+ in model tap water on corrosion behavior of A3003 was examined by immersion corrosion tests and galvanic corrosion tests. The immersed corrosion behavior is strongly depends on the buffer ability of the solutions, however, the kind of cation addition does not clearly affect on immersion corrosion behavior. The potential fluctuations and current fluctuations observed in galvanic corrosion tests show good correlation. A coexistence of Na^+ and K^+ in model tap water acts as corrosion inhibitor, on the other hand single existence of either ion does not inhibit corrosion of A3003.

(6) High wettability surface formed on Al by anodizng and drying and its corrosion resistance

The high wettability surface of aluminum was developed by the anodizing and desiccation treatment. The water contact angle of anodized samples increases with desiccation time, which indicates that desiccation is an effective method to achieve hydrophobicity of aluminum porous oxide film. The hydrophobic samples suffer little corrosion during a long period of immersion in

3.5 mass% NaCl solution. The rest potential in NaCl solution shows an order of hydrophobic sample, anodized samplem electropolished sample, which accounts for the corrosion resistance improvement of both anodizing and desiccation treatment. This can be explained by the interface area between solution and sample is reduced as the air-valley phenomenon, which may be the reason for the improved corrosion resistance.

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

Focusing pulse YAG laser beam irradiation (PRM) was applied to form area ratio, Sr, controlled model cut-edge on pre painted Zn and Zn- 55 mass% Al coated steels. A corrosion behavior of formed model cut-edge was investigated by wet/dry corrosion test. In high S_r of both specimens, red rusts are observed on steel substrate at model scratch. The dissolution of coated layer starts at the outer rim of scratched area and progresses into the zinc coating of under the paint of Zn coated steel. On the other hand, zinc rich phase of Zn - 55 mass% Al steel preferentially dissolved. Because of the preferential zinc rich layer dissolution, and formed longer corrosion area under the paint.

(8) Anodic reaction of titanium in artificial saliva by PRM

The electrochemical behavior of titanium was examined in artificial saliva by PRM (photon rupture method) and electrochemical methods. Rest potential is shifted to lower one by NaF addition in artificial saliva. Passive current increases with NaF addition in Fusayama-Meyre artificial salvia, but not in Hanks' balanced salt solution. This difference may be resulted from that in pH. Titanium reapassivates after oxide film removal by laser irradiation in NaF added simulated artificial saliva. The more NaF is added, the higher peak current density and amount of charge after laser irradiation become.

(9) Corrosion behavior of A2024 in shape controlled micro-pit

The purpose of this study is to form shape-controlled micro-pit on Al alloy by laser irradiation and to investigate the influence of shape on localized corrosion behavior on Al alloy via electrochemical measurement in micro-pit with different aspect ratio. To control laser irradiation time makes it possible to fabricate the artificial micro-pits with different aspect ratio. The aspect ratio of about 2 is obtained by 120 s laser irradiation. Rest potential at 2.4 ks after the pit fabrication becomes lower with increasing the aspect ratio of the fabricated pit. Repassivation ratio at 0.01 s after activation becomes lower with increasing the aspect ratio.

(10) Examination of corrosion behavior of 13Cr stainless steel in High Cl^- solutions.

The purpose of this research is corrosion behavior of low C -13%Cr stainless steel in high Cl^- solutions by electrochemical noise technique. A pitting potential decreases with increasing solutions temperature and the incubation time for pitting corrosion at constant potential decreases with increasing applied potential and with aeration of the solution. In single current fluctuation of non-growing pit, current increase slowly in proportion to 0.5, and decrease rapidly. An average PSD value at low frequency range and slope at high frequency range increase with increasing applied potential.

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

A new method for maskless fabrication of metal micro-rods or structures by solution flow type droplet cell, Sf-MDC. The developed Sf-MDC micro fabrication technique was applied to form Cu micro-rods or patterns on resin. To use 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 can be controlled by the deposition time. The conductivity of formed Cu micro-rods is about 11.8×10^6 Sm^{-1}. This technique also makes it possible to form both straight metal structures as well as branched, layered micro-rods and Cu deposit on resin. This fabrication technique can be applied to form resistance controlled micro wire or local surface treatment.

(12) Development local electrochemical analysis technique using Sf-MDC

A solution resistance reduced solution flow type micro-droplet cell with co-axial dual capillary tubes was developed to analyze local electrochemical behavior. A Pt counter electrode wire with 50 μm in diameter inserted in the inner capillary tube, successfully reduced solution resistance between the working and counter electrodes. The electrochemical performance of developed droplet cell is very similar to that of traditional macro size electrochemical cells. The Sf-MDC was applied to obtain line profiles of a current at a constant potential for cross-sections of model metal interfaces, and the current changed at the model interface of nickel and substrate, the spatial resolution of the developed droplet cell was reduced with increasing scanning speed of the cell.

(13) Formation of alumina nano-dots by LPD and anodizing

Liquid phase deposition, LPD, is direct oxide film formation technique from solutions. This technique makes it possible to form oxide film or oxide particle without post heating. Combined process of anodizing and LPD, make it possible to form oxide nano-dots, which have convex lens like shape. The purpose of this study is to investigate the influence on LPD and anodizing conditions on structure of formed oxide nano-dots. The nano-dots array can be formed on Al substrate.

(14) Local Oxide Film Formation on Al with Laser Irradiation and Anodizing in Ematal Bath

The localized formation of porous type oxide film on aluminum by anodizing in Ematal bath, laser irradiation, and re-anodizing is studied. The pore-sealing of the oxide film gave rise to a considerable improvement of the insulating properties of the anodic oxide film, showing a potential function similar to masks in Ematal bath. The oxide film was completely removed from the aluminum substrate by laser irradiation, and grooves with 70 μm width and 15 μm depth were fabricated. Anodic oxide film grows radially at the laser-irradiated area by re-anodizing. Formation of oxide film was not observed at areas that were not laser-irradiated, and this suggests good insulating properties of the pore-sealed oxide film formed by first anodizing.

(15) Effect of stress on oxide film structure and formation rate in model BWR condition

It is important to clarify role of thin oxide film on SCC in BWR or PWR environments. The initial oxide film structure and growth rate which were formed in model BWR environment were investigated by Raman spectroscopy, ellipsemetory and electrochemical impedance spectroscopy. The formed oxide film was Fe_3O_4,$\gamma-Fe_2O_3$, Fe-Cr spinel. The formation rate was increased with increasing applied stress.

Other activities

In May, Assoc. Prof. Sakairi attended 5th Kurt Schwabe Symposium in Electrochemistry held at the University of Erlangen-Nuremberg, Erlangen, Germany and presented paper entitled "Repassivation Behavior of Ti in Hanks Solution with PRM". After the symposium he visited Faculty of Materials Science and Ceramics, AGH-University of Science and Technology, Krakow Poland and meet Prof. Darek Kata and other professors in AGH-University of Science and Technology.

In September, Assoc. Prof. Sakairi attended Eurocorr 2009 held in Nice, France and presented paper entitled "Galvanic Corrosion Behavior of 3003 Aluminum Alloy in Model Tap Water."

In October, Assoc. Prof. Sakrairi attended 216th ECS held in Vienna Austria and presented papers entitled "Effect of surface condition and composition of solutions on repassivation behavior of titanium by PRM in vitro." and "Wet/Dry Cycle Corrosion Behavior of Model Cut-Edge Formed on Pre-painted Zinc Alloy

Coated Steels by Laser Fabrication."

In November Assoc. Prof. Sakrairi attended APGalva held in Jiju, Korea and presented paper entitled "Model Cut-Edge Formed on Zinc Coated Steels by Laser Machining and Its Corrosion Behavior."

Presentations

Synthesis and Application of Metal Nanomaterials Prepared in Flasks, Tetsu Yonezawa: Material Science Meeting, Hokkaido Univ., Sapporo, December 2009 (Invited)

Preparation of Copper Nanoparticles by Microwave Plasma in Lquid, Kunihiko Mori, Susumu Sato, Osamu Ariyada, Tetsu Yonezawa, Astsushi Hyono, Yoshio Okano: 3rd symposium of Japan Society of Electromagnetic Wave Energy Applications, Morito Memorial Hall, Tokyo University of Science, Tokyo, November 2009.

Cu Nano-/Fine-particles Covered by Polymer Nanoskin: Material for MLCC, Tetsu Yonezawa: ICAM 2009 (11th International Conference on Advanced Materials), Rio de Janeiro, Brazil, September 2009 (Invited)

Preparation of Aqueous Dispersion of Metal Nanoparticles and Applications for Inorganic/Organic Hybrid Resin, Yuichi Shishino, Tetsu Yonezawa, Hiroshi Nishihara, Kaname Hase, 62nd Annual Meeting of the Division of Colloid and Interface Surface, CSJ, Okayama University of Science, Okayama, September 2009.

Preparation of Extremely Small Metal Nanoparticles and Their Luminescent Properties, Yuichi Shishino, Tetsu Yonezawa, Koji Kawai, Hiroshi Nishihara, 58th Symposium of the Society of Polymer Science, Japan, Kumamoto University, Kumamoto, September 2009.

Wet Preparation of Metal Nanoparticles and Applications, Tetsu Yonezawa, 2009 Meeting of Mining and Metallurgical Institute of Japan, Hokkaido University, Sapporo, September 2009 (Invited).

Quantitative Calculation of Interactions of Blood Cells, Atsushi Hyono, Toshio Matsuda, Hiroyuki Ohshima, Tetsu Yonezawa, Summer Session of Hokkaido Branch, Chemical Society of Japan, Tomakomai Kosen, Tomakomai, July 2009

Preparation of Gold Nanoparticle-Dispersed Transparent Resin and Its Optical Property, Yuichi Shishino, Tetsu Yonezawa, Hiroshi Nishihara, Summer Session of Hokkaido Branch, Chemical Society of Japan, Tomakomai Kosen, Tomakomai, July 2009

Effect of F^- ions on repassivation of Ti in Hank's, M. Kinjyo, M. Sakairi and T. Kikuchi, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, Jan., 2009.

Formation of model pit on Al and its corrosion behavior, K. Yanada, M. Sakairi and T. Kikuchi, ibid.

Effect of current on fabrication of Cu structure by Sf-MDC, R. Goto, M. Sakairi and T. Kikuchi, ibid.

Metal patterning by using Pd catalyst and Laser ablation, Y. Wachi, T. Kikuchi and M. Sakairi, Winter Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2009.

Localized Ni patterning by using Pd catalyst and Laser irradiation, Y. Wachi, T. Kikuchi and M. Sakairi, The 119th Surf. Fin. Soc. Jpn. spring meeting, Yamanashi, March, 2009.
Formation of micro-Cu rod by modified Sf-MDC, Y. Goto, M. Sakairi and T. Kikuchi, ibid.

Effect of cation on corrosion of A3003 in model tap watere, M. Sakairi, A. Kaneko, T. Kikuchi, 144th spring meeting of Jpn. Inst. Metals, Tokyo, March, 2009.

Formation of model cut-edge on pr-coated steel and its corrosion behavior, M. Sakairi, A. Kageyama and T. Kikuchi, ibid.

Electrochemical behavior of newly developed Sf-MDC, M. Sakairi, T. Murata and T. Kikuchi, The Spring meeting of ISIJ, Tokyo, March, 2009.

Localized dissolution of Fe by Sf-MDC, T. Murata, M. Sakairi and T. Kikuchi, The 76th Meeting of the Electrochem. Soc. of Jpn., Kofu, March, 2009.

Formation of oxide nano-dots on Al by LPD and anodizing, R. Fujita, M. Sakairi and T. Kikuchi, ibid.

Effect of PWHT on electrochemical behavior of low C - 13%Cr welded joints by using solution flow type micro-droplet, S. Hashizume, T. Nakayama, M. Sakairi and K. Fushimi, Corrosion 2009, Atlanta Grogea, March, 2009.

Fabrication of model pit on A2024 by laser irradiation and its corrosion behavior, M. Sakairi, K. Yanada and T. Kikuchi, Spring meeting of Light metal soc., May, Noboribetsu, 2009.

Repassivation kinetics of Ti at repeated irradiation in Hanks solution by PRM, M.

Kinjyo, T. Kikuchi and M. Sakairi, Zriryo-to-Kankyo2009, May, Tokyo, 2009.

Fabrication of model pit on 2000 Al alloy by laser irradiation and its corrosion behavior, K. Yanada, M. Sakairi and T. Kikuchi ibid.

Investigation of effect of initial surface conditions on field crystallization of Al anodic oxide film with synchrotron X-ray diffraction, M. Sakairi, T. Kikuchi, D. Nagasawa and T. Suda, ASST2009, Leiden, May, 2009.

Formation of micro-pits on al alloy with PRM and initial stage of localized corrosion in the formed pits, M. Sakairi, K. Yanada, T. Kikuchi, Y. Oya and Y. Kojima, ibid.

Repassivation Behavior of Ti in Hanks Solution with PRM, M. Sakairi, M. Kinjyo and T. Kikuchi, KSCS2009, Erlannge, Germany, June, 2009.

Formation of semi-speher alumina structure by LPD and anodizing, R. Fujita, M. Sakairi, H. Jha and T. Kikuch, Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Tomakomai, July, 2009.

Micro-fabrication on metal surface by Sf-MDC, T. Murata, M. Sakairi and T. Kikuchi, ibid.

Electrochemical behavior of stainless steel in acid NaCl solutions, J. Tatehara, M. Sakairi and T. Kikuchi, ibid.

Galvanic corrosion behavior of 3003 Aluminum alloy in model tap water, M.Sakairi, A. Kaneko,T. Kikuchi, Y. Seki, and D. Nagasawa, Eurocorr 2009, Nice, September, Farance, 2009.

Electrochemical mixed process for micro-fabrication of Al, Y. Wachi, T. Kikuchi, M. Sakairi and T. Yonezawa, The 120th annual meeting of J. Soc. Sarf. Fin., Makuhari, September, 2009.

Localized anodizing of aluminum in Ematarl solution, S. Fujita, T. Kikuchi, M. Sakairi and T. Yonezawa, ibid.

Local metal deposition on resin by new type Sf-MDC, Y. Goto, M. Sakairi and T. Kikuchi, ibid.

Effect of working distance on micro-fabrication by Sf-MDC, T. Murata, M. Sakairi, T. Kikuchi and K. Fushimi, The 2009 autumn meeting of the Electrochem. Soc. of Jpn., Tokyo, September, 2009.

Formation hemisphere alumina dots by LPD and anodizing, R. Fujita, M. Sakairi, H. Jha and T. Kikuchi, ibid.

Galvanic corrosion of A5000 in model tap water, M. Sakairi, A. Kaneko, T. Kikuchi, Y. Seki and D. Nagasawa, The 145th autumn meeting of Jpn. Inst. Metal, Kyoto, September, 2009.

ENA of 13%Cr in acid NaCl solutions, J. Tatehara, M. Sakairi, T. Kikuchi and S. Hashizume, The 56th Jpn. Conf. on Materials and Environments, Osaka, September, 2009.

Anodic dissolution of Ti in artificial saliva by PRM, M. Kinjyo, M. Sakairi and T. Kikuch, ibid.

Changes of restpotensial in model pit formed in Al alloy by PRM, K. Yanada, M.

Sakairi, T. Kikuchi, Y. Oya and Y. Kojima, ibid.
Wet/Dry Cycle Corrosion Behavior Of Model Cut-Edge Formed On Zinc Coated Steels By Laser Fabrication, M. Sakairi, A. Kageyama and T. Kikuhci, The 216th ECS Meeting, Vienna, Austria, October, 2009.

Effect of Surface Condition and Composition of Solutions on Repassivation Behavior of Titanium by PRM in Vitro, M. Sakairi, M. Kinjyo, H. Miyata and T. Kikuchi, ibid.

ENA of Galvanic Corrosion of A5052 in Model Tap Water, M. Sakairi, A. Kaneko, The 117th meeting of Light Metal Soc., Tokyo, November, 2009.

Model Cut-edge Formed on Zinc Coated Steels by Laser Machining and Its Corrosion Behavior, M. Sakairi, A. Kageyama and T. Kikuchi, APGalva2009, Cheju, Korea, November, 2009.

Anodic Oxidation of the Inner Wall of the Microchannel Formed by Ti-Al Reactive Infiltration, M. Ishida, T. Ohmi, M. Sakairi and M. Iguchi, 4th ISEM2009, Niigata, November, 2009.

Facilities and Capabilities

Transmission Electron Microscopy, Hitachi 300kV
Focused Ion Beam, Hitachi
Field Emission Scanning Electron Microscopy, JEOL
ζ-potential and DLS measurement. Ohtsuka Denshi
Centrifuge: Beckman
Microcentrifuge: TOMY
Ultracentrifuge: Hitachi
Dry Box: Miwa

Evaporator: EYELA
RO Water Purifier: ELGA
Vacuum Drying Oven: YAMATO
Magnetron Sputtering Apparatus: Shinkuu Device
UV Spectrometer: JASCO
IR Spectrometer: Shimadzu
Fluorescence Spectrometer: JASCO
DSC: Rigaku
TG-DTA: Shimadzu
AFM: SII
Atmospheric Plasma in Liquid: ARIOS
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.

ADVANCED COATING LABORATORY

Specially Appointed Professor Dr. Toshio Narita
Tel.:+81-11-706-7208 Fax.:+81-11-706-7208
E-mail:narita@eng.hokudai.ac.jp
Visiting Professor Dr. Masaharu Nakamori
Visiting Associate Professor Dr. Takayuki Yoshioka
Visiting Assistant Professor Dr. Saiko Ohta

Secretary

Ms. Mayumi Ara

Researchers

Dr. S. Konda, Dr. S. Koyama, M. Eng. M. Ohtsuka

Technical Staffs

Mr. T. Tagawa, Ms. M. Sekine, Ms. K. Suetomi, Ms. Y. Oishi, Ms A. Yoneya, and Ms C. Kawashima

Visiting Researchers

Dr. K. M. Zaini (LIPI, Indonesia)
Dr. T. Izumi (Hitachi Co. Ltd.)
Mr.S. Harashima (Nittobo Co. Ltd.)

The Specially Promoted Research (2006-2010) supported by Japanese Government has been finished by end of March, 2010. A new laboratory was established on advanced coatings, supported by Nittobo Co. Ltd., for term of three years (2010/07~2012/06), focusing on research and development of novel diffusion barrier coating systems to improve high temperature capabilities of ultra high temperature materials.

This research projects 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) R & D of novel DBC systems to refractory metals such as Nb, Mo, and W.
2) Application of the DBC system to Ni base SC superalloy for land base gas turbines,
3) Application of the DBC system to Ni-based alloys and Fe-based alloys
4) Understanding high temperature oxidation and corrosion behavior of alloys and coatings.

Presentations

T.Narita: Creep and oxidation behavior of heat-resistant alloys with diffusion barrier coating system, The 12th International Conference on Fracture, Ottawa, Canada, 2009.7.15

T. Narita: The use of diffusion barrier coating system to extend the life of β-phase and γ' + γ coatings under cyclic oxidation, Gordon Research Conference - High Temperature Corrosion, New London, USA, 2009.7.29

T. Narita: Diffusion coating of Hf and Al on Ni-base alloys by co-packing process, ASEAN-INDIA Workshop and Annual Meeting on Surface Engineering -2009, Bandung, Indonesia, 2009.12.1

AFFILIATE MEMBERS

AFFILIATE MEMBER

Prof. Dr. Kazuhisa Azumi
TEL/FAX: +81-11-706-6747
Email: azumi@eng.hokudai.ac.jp

Students

Takeshi Sakamoto, Atsushi Naganuma, Jinwei Tang, Jun Kanno, Takayuki Nosaka, Yuto Aoki, Yusuke Sato, Jungo Yajima

PD

Elsentriecy Hassan Hamed

Our group has intended to explore the fundamental corrosion mechanism of metals, development of corrosion monitoring system, surface finishing of aluminum and magnesium alloys and corrosion related phenomena in fuel cell.

Current topics on research are in the following:

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

Mg and its alloys are attractive materials because of its light weight, high strength and bountiful resource. On the other hand high corrosion susceptibility of them limits their application. Various surface coating techniques have been, therefore, developed. To clarify the suitable condition for electrodeposition of corrosion resistive Al coating of Mg, Al was electrodeposited on a Pt substrate from ionic liquid bath of EMIC containing $AlCl_3$ using various kind of polarization method including pulse method. Smooth and good adhesive Al coating was obtained using bipolar current pulse method after optimization of duty ratio and intensities of anodic and cathodic current.

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

Saltery plant has been operated under highly corrosive condition, i.e., aqueous environment containing saturated sodium chloride at high temperature more than 100 °C. Crevice corrosion is specially severe in this plant even for very-high corrosion-resistive super stainless steels. Distribution of coupling current inside and outside of crevice made in various stainless steel specimen was thus measured using multichannel electrode system in the condition simulating saltery plant. The specimen constructed from five sheets of SUS316L, NAS64, NAS185N and NAS254N stainless steels with small holes treated as crevice was immersed in saturated NaCl solution at high temperature up to 100 °C. Distribution of anodic and cathodic coupling current and its transition in time and space depend on kind of alloy, temperature, and supply of dissolved oxygen, and coverage of the surface with corrosion product or passive film.

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

Copper is one of candidate metal for overpack container of radioactive nuclear wastes produced in atomic power plant to be stored deep-underground to separate them from civil environment. Temperature-compensated resistometry method was applied to evaluate corrosion rate of copper in repository condition. A couple of Cu films with thickness of 5 μm 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 °C. Relative resistance change of corroded 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. Composition and amount of corrosion products was also evaluated from time variation of electrode potential during the galvanostatic cathodic reduction of corroded specimen and compared with the results obtained by resistometry.

(4) Photoelectrochemical property of Zn-Al plating layer on steel

Zinc plated steel has been widely used as base material in various structures. Use of zinc should be, however, reduced because of its limited resource and thus the performance of corrosion protection property of Zn plating layer alloyed with other metals such as Al, Mg and Si has been evaluated. In this study fundamental property of oxide film formed on plating film of ZnAl alloy was evaluated using electrochemical polarization, photocurrent spectroscopy and impedance spectroscopy measurements. For example, property of oxide film on ZnAl alloys altered gradually from an n-type semiconductive film formed on Zn to dielectric film formed on Al with increase in Al content in the alloy. Contribution of semiconductive or dielectric property to the oxide film depended on not only composition of the film but also duration of anodic oxidation and addition of Cl^- ion to the solution.

(5) Fabrication of proton conductive pseudoboehmite thin film

In PEFC system a perfluorosulfonic acid membrane called Nafion® has been used as a PEM (Proton Exchange Membrane) because of its highly proton-conductive property provided by a small amount of water contained in the micro-pore of membrane. Operation temperature of PEFC system is ordinary limited lower than 100 °C to hold water in the membrane although higher operation temperature is desirable for better power geneartion efficiency and for reduction of expensive catalysts. In this work, therefore, proton conductivity pseudoboehmite thin membrane was fabricated for use as a PEM. Al foil was electrochemically oxidized to form porous anodic oxide film, immersed in boiled water to convert the surface of oxide to pseudoboehmite and then the substrate metal and barrier oxide layer was removed by acidic etching from backside. The membrane obtained was then deposited with Pt on both sides and built into FC type cell. This membrane exhibited voltage response to H_2 gas supply although the value is considerably small.

Presentations

A. Naganuma, K. Azumi: Application of Multi-channel Electrode System on Corrosion Research; Corrosion Dream 2009, Electrochemical Society of Japan, Dec., 2009, Sapporo.

J. Kanno, K. Azumi: Effect of Additives on Ni Electrodeposits, *ibid*.

K. Azumi , A. Naganuma: Crevice Corrosion Monitoring of Stainless Steel in the Environment Simulating Saltely Plant; 56th Annual meeting of Japan Society of Corrosion Engineering, Sep., 2009, Osaka.

K. Azumi, F. Nishiyama, H. Konno: Fabrication of Optical Fiber pH Sensor using Porous Anodic Oxide Film of Al; The 120th Annual Meeting of Surf. Finish. Soc. Jpn., Sep., 2009, Makuhari.

K. Azumi, Y. Tomita, K. Fushimi: Improvement of pH Response of Ir Oxide electrode; *ibid*.

K. Azumi: Corrosion Measurement of Metals in Saltely Plant using Multichannel Electrodes Method; The 21st meeting of research grand by the salt science research fundation, July, 2009, Tokyo.

K. Azumi, A. Naganuma, T. Nosaka and K. Fushimi: Principle and Application of Multichannel Electrode System In Corrosion Research; KSCS2009, May, 2009, Erlangen.

J. Kanno, K. Sakamoto, S. Hayashi, K. Azumi: EBSD Analysis of Additive Effect on Crystallographic Orientation of Ni Plating Layer; 76th Annual Meeting of Electrochemical Society of Japan, March, 2009, Kyoto.

T. Nosaka, K. Azumi: Size Effect of Al Surface Area on Electroless Ni Plating and Zincate Pretreatment; *ibid*.

A. Naganuma, K. Azumi: Analysis of Corrosion Behavior and Mass Transfer as a Function of Spatial Orientation and Dimension of Artificial Crevice using

Multichannel Electrode Method; The 119th Annual Meeting of Surf. Finish. Soc. Jpn., March, 2009, Kofu.

J. Kanno, T. Sakamoto, S. Hayashi and K. Azumi: Analysis of effect of additives on crystalline orientation of Ni plating by EBSD (Poster); EICCS2009, March, 2009, Sapporo.

A. Naganuma, K. Azumi: Analysis of Corrosion Behavior and Distribution of Chemical Species as a Function of Artificial Crevice Shape using Multichannel Electrode Method; Winter Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2009, Sapporo.

F. Nishiyama, H. Konno, K. Azumi: Optimization of pH Sensitive Membrane using Porous Anodic Oxide Film formed on Al; *ibid*.

J. Kanno, K. Sakaomoto, S. Hayashi, K. Azumi: Effect of Additives on Crystallographic Orientation of Ni Electroplating Layer using EBSD; *ibid.*

Y. Tomita, K. Fushimi, K. Azumi: Development of Micro-pH Sensor (Poster); *ibid.*

T. Nosaka, K. Azumi: Size Effect of Al Surface Area on Zincate Pretreatment (Poster); *ibid.*

AFFILIATE MEMBER

Prof. Dr. R. O. Suzuki
Tel.:+81-11-706-6339 Fax.:+81-11-706-6342
E-mail:rsuzuki@eng.hokudai.ac.jp

Students

M. Baba, Y. Sasaki, D. Yamada, S. Osaki, K. Watanabe,
K. Otake, N. Kobayashi, T. Takahashi, R. F. A. Descaller,
H. Nashiyama, R. Enmei, I. Ueda and T.Fujisaka

Prof. Ryosuke O. Suzuki merged as the professor of the laboratory of Eco-processing from Kyoto University on March 2006. He began to study the non-ferrous metallurgy based on the molten salt electrolysis.

The research activities of the group 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 corrosion 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.

Prof. R.O. Suzuki was invited at the International conference on Thermoelectrics (ICT2009) which was held at Freiburg, Germany, May 2009. He talked on the fluid dynamic simulation for thermoelectric energy conversion. Prof. R.O. Suzuki made an invited lecture at Tokyo in April on preparation of vanadium based hydrogen storage alloys based on the electrolysis at a high temperature. He was invited as keynote lecturer at the 18th international conference on Processing and Fabrication of Advanced Materials (PFAM XVIII) at Sendai, Japan. He talked on the calciothermic reduction using molten $CaCl_2$ and electrolysis to produce the noble metals such as titanium and tantalum.

The following foreign scientists visited this laboratory: Prof. Geir Martin Haarberg, Norwegian University of Science and Technology, Trondheim, Norway. Ms Reyna Famila Descallar joined us from Mindanao State University, Philippines, as a master student in e3 class.

Presentations

Silent Discharge under Ambient Pressure of Air for Nitrization of Pure Metals, S. Akiyama, K. Watanabe and R.O. Suzuki: The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jan. 2009.

Reduction and Synthesis of Biomedical Ti-29Nb-13Ta-4.6Zr alloy by the Molten Salt Electrolysis of ($CaCl_2$+CaO), S. Osaki, 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., Muroran, Jan. 2009.

Synthesis of vanadium based hydrogen storage alloys, R.O. Suzuki : The 52th Annual Meeting of Materials Tailoring, Tokyo, Apr. 2009.

Optimal Fluid Conditions on Thermoelectric Power Generation Using Multi-Panels, Y. Sasaki and R.O. Suzuki: The Summer Joint Meeting of The

Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul. 2009.

Thermoelectric Properties of Ternary Compounds Zr_3Mn4Si_6 and $TiMnSi_2$; R.O. Suzuki and H. Kozasa : The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Jul. 2009.

Thermoelectric Properties of Low Conductive Compounds: Zr_3Mn4Si_6 and $TiMnSi_2$; R.O. Suzuki and H. Kozasa : Int. Conf. of Thermoelctrics, Freiburg, Germany, Jul. 2009.

Optimal Fluid Direction in the Paths among Thermoelectric Multi-Panels ; R.O. Suzuki and Y. Sasaki : Int. Conf. of Thermoelctrics, Freiburg, Germany, Jul. 2009.

Optimized Flow Path Condition for the Multi-flat Panel Thermoelectric Generation Systems ; Y. Sasaki and R.O. Suzuki : 6th Annual Meeting of Jpn. Thermoelctric Soc., Freiburg, Germany, Jul. 2009.

Electrolysis of Titanium Oxides and Experimental Phase Diagram ; K. Kobayashi and R.O. Suzuki : Annual Meeting of Jpn. Inst. Metals, Kyoto, Sept. 2009.

Crystallization of Desulfuric Slag ; Y. Kusada, R.O. Suzuki and Y. Kashiwaya : Annual Meeting of Iron and Steel Inst. Jpn., Kyoto, Sept. 2009.

Carbon Resourcing by Molten Salt Electrolysis and Reduction of CO_2 Gas at High Temperature ; H. Sakai, K. Ohtake and R.O. Suzuki : 41th Symp. on Molten Salt Chemistry, Kyoto, Nov. 2009.

Reduction of Titanium Oxide in OS Process and its Reducing Paths ; K. Kobayashi, Y. Kobayashi and R.O. Suzuki : 41th Symp. on Molten Salt Chemistry, Kyoto, Nov. 2009.

Direct Reduction of Ti-29Nb-13Ta-4.6Zr Alloy by Calciothermic Reduction in the Molten $CaCl_2$; S. Osaki, H. Sakai and R.O. Suzuki : 41th Symp. on Molten Salt Chemistry, Kyoto, Nov. 2009.

Solubility and Dissolution Behavior of $TiCl_4$ Gas into the Molten $CaCl_2$; J. Hashidume and R.O. Suzuki : 41th Symp. on Molten Salt Chemistry, Kyoto, Nov. 2009.

Direct Reduction of Ti-29Nb-13Ta-4.6Zr Biomedical Alloy from Oxide Mixture in Molten $CaCl_2$; S. Osaki, H. Sakai and R.O. Suzuki : 18th international conference on Processing and Fabrication of Advanced Materials (PFAM XVIII), Sendai, Dec. 2009.

Direct Metal Production from Oxides by Using Molten Salt Electrolysis of CaO in $CaCl_2$; R.O. Suzuki : 18th international conference on Processing and Fabrication of Advanced Materials (PFAM XVIII), Sendai, Dec. 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.

Oxygen and Nitrogen Analyzer: LECO TC-600. Inert gas extraction with carbon crucible and infrared absorption method, 5mass%-0.05 mass ppm. The previous set was replaced to the most modern.

Sulfur and Carbon Analyzer: LECO CS-600. Carbon and nitrogen are converted to CO and NO gas by burning in O_2 gas with RF heating and they are detected by the infrared absorption method. 6mass%-0.6 mass ppm. The previous set was replaced to the most modern.

CO/CO_2 Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 10 vol%.

NO/SO_2 Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 2 vol%.

Constant voltage generators: Takasago Electrics. 4 sets. Max.50V and 20 A.

High voltage amplifier: Takasago Electrics. 100V-8000V.

Ozone gas generators: 2 sets. max 8 vol%O_3 gas using O_2 gas.

Thermal Analyzers: SII EXSTAR-6000 TG/DTA. With Pt heater up to 1500C. The previous apparatus was renewed.

Thermal Conductivity Measuring Unit: Kyoto Electrics. Hot disk method at room temperature.

AFFILIATE MEMBER

Assoc. Prof. Dr. Koji Fushimi
TEL./FAX: +81-11-706-6737
E-mail: kfushimi@eng.hokudai.ac.jp

Students

T. Yamamoto, K. Matsushita, A. Ono, K. Miyamoto, H. Watanabe

The research activities of the laboratory are directed to the materials surface science and engineering. We are interested in the micro-electrochemistry for a better understanding of the interfacial phenomena of metal and semiconductor electrodes in relation to electrochemical devices, corrosion, passivation, and surface finishing.

Current topics on research are as follows:

(1)Micro-indentation Test for Depassivation-repassivation of Metal Surfaces

Micro-indentation test of the iron surface in boric-borate solutions was carried out to investigate the mechano-electrochemistry of depassivation and repassivation. The indentation could deform the surface either or both elastically or plastically, and the electrochemical measurement was used to analysis the current flowing for repassivation following to depassivation. A series of tests were applied to investigate the dependence of the mechanism and kinetics of depassivation-repassivation on the deformation manner, the conductivity and pH of the solution, the hardness of the specimen substrate, and the thickness of the passive film.

(2) Modification of Flowing-electrolyte Type Micro-droplet-cell

Flowing-electrolyte type micro-droplet-cell (f-MDC) developed for the micro-electrochemistry was modified to improve the stability of current flowing in the cell, the facility of the cell fabrication, and the lateral resolution in the scanning

MDC application. Instead of a coaxial double capillary used in the conventional f-MDC, a multi-channel capillary, that was composed of an inner channel and six outer cannels for the supply fresh electrolyte and for the remove used electrolyte, respectively, was developed and applied to probe the local electrochemical reactivity on the aluminum alloy and so on. The effect of oxygen dissolving from the meniscus between the droplet and specimen surface was also discussed in detail.

(3) Anisotropic corrosion of iron in pH 1 sulphuric acid

Anisotropic corrosion behaviour of a single grain of pure iron in 0.05 mol dm^{-3} sulphuric acid (pH 1) was investigated by a simple polarization technique. Both corrosion potential and corrosion current were found to be dependent on crystallographic orientation of the iron grain. A high corrosion current flowed on a grain showing a relatively noble corrosion potential, although both cathodic and anodic Tafel slopes were independent of the orientation. It was shown that cathodic hydrogen evolution reaction (HER) governed the corrosion reaction on the iron grain. Covalent bonding of Fe and H and coverage of H on Fe seem to play important roles in the HER and anisotropic corrosion behaviour of pure iron.

(4) Development of Coaxial Double Ring Microelectrode for the Probe of a Scanning Electrochemical Microscope

Heating treatment of quartz capillaries with town gas was applied to fabricate the probe electrode of a scanning electrochemical microscope (SECM). The treatment enabled to coat the electrically conductive carbonaceous layer with a thickness of several hundreds nanometers on both inner and outer walls of the quartz substrate. After the suitable coating the wall surfaces with insulating polymer resin, the capillary tip was polished to obtain the ring electrodes. From the measurement of the limiting current in the redox mediator, we could confirm that the typical diameter of the electrode was less than 1 micrometer. The fabrication process of the electrode is highly reproducible and is useful to the further micro-electrochemistry such as SECM.

(5) Carbonaceous Layer Coating on Type-316 Stainless Steel Plate for PEFC Bipolar Plate

A simple method to coat the carbonaceous layer on SUS316 stainless steel plate was developed. The plates were put in an alumina boat with powder of petroleum pitch A240F separately and heated at 1073–1273 K under flowing pure argon. By this process, plates were coated with a uniform carbonaceous layer. The electric-conductivity of the layer and the corrosion resistance were improved by the increase in the heating temperature and by the pretreatment of the steel plate surface. After the electroplating of nickel, the layer showed a high electric-conductivity. It was indicated that the inhibition of oxide formation in the layer plays an important role for the good conductivity as well as corrosion resistance.

Other Activities

In September, Dr. Koji Fushimi attended to EuroCorr 2009 held in Nicer, France, and presented the paper entitled “Mass Transfer Controlling Reaction in Flowing Electrolyte-type Micro-droplet Cell”. In October, Dr. K. Fushimi and Mr. Takatoshi Yamamoto attended to The 216th Annual Meeting of Electrochemical Society held in Vienna, Austria, and presented the papers entitled “Anodic Dissolution of Titanium in Ethylene Glycol Solution Containing Chloride Salt” and “Effect of Cold-rolling on Passive Film on Pure Iron in pH8.4 Borate Buffer Solution”, respectively. They also visited Johannes Kepler Universität Linz, Austria, and discussed with Professor Achim W. Hassel.

Presentations (international symposia)

K. Fushimi, S. Yamamoto, H. Habazaki, H. Konno; “Hydrodynamic Effects in Flowing Electrolyte-type Micro-droplet Cell”, International Symposium International Symposium for Environmental Innovation Driven by Chemistry and Catalytic Science (EICCS 2009), Mar. 18-19, Sapporo (2009).

T. Yamamoto, K. Fushimi, H. Konno, S. Miura; “Effect of Cold-rolling on Passivation of Pure Iron in pH8.4 Borate Solution”, International Symposium International Symposium for Environmental Innovation Driven by Chemistry and Catalytic Science (EICCS 2009), Mar. 18-19, Sapporo (2009).
M. Seo, K. Fushimi, H. Habazaki, and T. Nakayama; “Polarization Behavior of

Nickel in Acidic Perchlorate and Acetate Buffer Solutions Containing Small Amount of Pb^{2+}", 60th Annual Meeting of the International Society of Electrochemistry, Aug. 16-21, Beijing, China (2009).

K. Fushimi, S. Yamamoto, H. Habazaki, H. Konno, "Mass Transfer Controlling Reaction in Flowing Electrolyte-type Micro-droplet Cell", EuroCorr 2009, Sep. 6-10, Nice, France (2009).

T. Yamamoto, K. Fushimi, H. Konno, "Current Transients from Anodized Aluminum Surface Using Micro-indentation Test", The 3rd GCOE International Symposium Catalysis as the Basis for the Innovation in Materials Science –Beyond the Horizon of Materials Chemistry–, Sep. 14-15, Sapporo (2009).

K. Fushimi, H. Kondo, H. Konno, "Anodic Dissolution of Titanium in Ethylene Glycol Solution Containing Chloride Salt", The 216th Annual Meeting of Electrochemical Society, Oct. 6-10, Vienna, Austria (2009).

T. Yamamoto, K. Fushimi, S. Miura, H. Konno, "Effect of Cold-rolling on Passive Film on Pure Iron in pH8.4 Borate Buffer Solution", The 216th Annual Meeting of Electrochemical Society, Oct. 6-10, Vienna, Austria (2009).

ABSTRACTS of PUBLICATIONS

Passive Oxide Films and Their In-situ Detection

Toshiaki Ohtsuka

Proc. International Conf. on Materials Engineering for Resources (ICMR) 2009,
189 (2009)

The passive oxide film electrochemically formed on iron was investigated by in-situ ellipsometry and Raman spectroscopy. The thickness of the passive oxide on iron increases with potential under both stationary and non-stationary conditions. The growth may be followed by the field-assisted ionic migration mechanism coupled with non-stationary dissolution of ferric ions from the oxide. From spectroscopic ellipsometry, a light-absorption edge was estimated at 2.6 eV, which may be a band gap energy of the semiconducting passive oxide. When Fe^{2+} ions exist in the solution, the anodic deposition of $FeOOH \cdot H_2O$ takes place, resulting in formation of an outer hydrous layer a few 10 nm thick. The Raman spectra of the passive oxide correspond to those of Fe_3O_4 and γ-Fe_2O_3.

In-situ Raman Spectroscopy for the Passive Oxide Film on Iron in Neutral Borate Solution

Toshiaki Ohtsuka, Kento Taneda

ECS Trans., **16**, 125-131 (2009)

In-situ Raman spectra of the passive oxide film in neutral borate solution at pH 8.4 was measured without any enhancement such as surface enhanced Raman scattering or resonance Raman scattering. To measure the Raman spectra of the surface thin film on the electrode, we introduced a confocal collection system to reject the scattering signal from the electrolytes surrounding the surface in front of the spectrometer. The background signal is still high, and it is more intensive by 100 times than the Raman signal from the passive film. The difference Raman signal between the surfaces of the passivated iron and the reduced bare iron reveals a peak at about 670 cm^{-1}. When we measured the passivated iron surface soon after transfer from the electrolytes to air, we observed another broad and faint peak at 320 cm^{-1}. From these peaks, we assume that the passive oxide film on iron is composed of Fe_3O_4 and γ-Fe_2O_3

Self-healing Ability of Conductive Polypyrrole Coating with Artificial Defect

D. Kowalski, M. Ueda, T. Ohtsuka

ECS Trans, **16** (52), 177-181 (2009)

A bi-layered PPy film consisting of an inner layer doped with keggin-structure anions of $PMo_{12}O_{40}^{3-}$ and HPO_4^{2-} (PPy-PMo^{12}) and an outer layer doped with organic anions of dodecyle sulfate (PPy-DoS) exhibited a self-healing property when coated on steel. When a defect was introduced into the PPy-coated steel immersed in 3.5 % NaCl aquesous splution, the potential initially dectreased and activation of the coated steel occurs. After a few hours, the potential was recovered to the passive region, and passivation conyinued for another 20 hours. Without any damage, the release of PMo_{12} doped in the inner layer, was inhibited by the outer PPy layer doped with DoS. When a defect was introduced into the PPy film, the inner PPy layer released phosphate and molybdate anions to the damaged zone due to their decomposition via hydrolysis. Both anions work as passivation inhibitors and helped to repassivate the damaged zone on the steel.

Ion-Exchange Treatment of Glass Surface in $NaNO_3$ - $TlNO_3$ Molten Salt

Yasushi TABEI, Mikito UEDA, Toshiaki OHTSUKA, Toshiharu YAMASHITA

Electrochemistry, **77**, 709-712 (2009)

To make functional glasses, ion-exchange treatment of the glass surface was carried out in $TlNO_3$-$NaNO_3$ molten salt at 673 K and 723 K for various time periods, and then the Tl ions embedded in the glass were reduced to metallic Tl nanoparticles by hydrogen gas. The color of the glass containing metallic Tl nanoparticles changed to brown or black. The Tl nanoparticles were detected by a qualitative TEM analysis. The optical absorption spectra of these treated glasses showed a peak at about 370 nm. With increases in the temperature of the molten salt, the band intensity of the absorption is enhanced. The absorption increase may correspond to larger particle sizes and densities with the increase in temperature. The Tl nanoparticles with 10-150 nm diameter were observed at neighboring parts of the glass surface by TEM and FE-SEM.

Electrodeposition of Bi-Sb-Te Alloys By Pulse Electrolysis in $AlCl_3$-NaCl-KCl Molten Salt

Mikito UEDA, Shoh TSUCHIYA, and Toshiaki OHTSUKA

Electrochemistry, **77**, 659-662 (2009)

The Electrodeposition of Sb-Bi-Te alloy in $AlCl_3$–NaCl–KCl molten salt containing $SbCl_3$, $BiCl_3$, and $TeCl_4$ at 423K was carried out under constant potential control and potential pulse control in the melt. The electrodeposition results show that the $SbCl_3$ concentration is effective to control the composition of Bi-Sb-Te ternary alloy. The electrodeposited $Bi_{0.5}Sb_{1.5}Te_3$ by pulse electrolysis with frequency = 100 Hz and D.R.(Duty Ratio) = 75 %, had good crystallinity and the preferential orientation of the electrodeposit was the (110) plane in this electrodeposition experiments. The electrodeposit had homogeneous disk-like granules. The power factor of the electrodeposit was calculated as 3×10^{-5} $Wm^{-1}K^{-2}$ from the Seebeck coefficient and the electrical conductivity.

Electrorefining Reaction of Sodium in Propylene Carbonate Containing $NaPF_6$

Mikito Ueda, Hideki Hayashi, and Toshiaki Ohtsuka

J. Japan. Inst. Metals, **73**, 691-694(2009)

To develop a sodium electrorefining process for the recycling of used sodium-sulfur secondary battery, a non-aqueous electrolytic melt was investigated to pursue an efficient solvent and electrolyte for the process. Propylene carbonate containing $NaPF_6$ was selected, since it has a wide potential window for electrochemical stability and a weak reactivity with metallic sodium. From the impedance measurement of propylene carbonate containing $NaPF_6$, the maximum electric conductivity of 75 mS cm^{-1} was found at concentration of 1 M $NaPF_6$ at 338 K. The cathodic deposition of metallic sodium on a glassy carbon electrode and the anodic dissolution of metallic sodium occurred in the electrolytic melt. Sodium and a small amount of phosphorus were detected in the electrodeposit by ICP-AES analysis. (Japanese)

Removing of Mg in Al-Mg Alloy by Calcined Powder from Used Dry-cell Batteries

Mikito Ueda, Yasutaka Ta, Toshiaki Ohstuka, and Hidenori Takahashi

J. Japan. Inst. Metals, **73**, 773-777(2009)

To reduce Mg content in Al-Mg alloy for aluminum recycling, calcined powder made from used dry-cell battery was reacted with the liquid aluminum alloy. The powder was found to consist of $ZnMn_2O_4$, MnO, ZnO, and carbon by XRD analysis. After the reaction between pellets of the powder and the alloy in liquid at 973K or 1073K for 3.6×10^3s, Mg content in the alloy decreased from 4.0 to 2.3 mass%. And at the same time, contents of Mn and Zn in the alloy increased from 0 to about 0.2 and 0.1 mass%, respectively. During the reaction, metallic Mg in the liquid Al-Mg alloy was found to move in to the pellets to form MgO. It may be assumed that an exchange reaction between Zn^{2+} at ZnO in the pellets and Mg^{2+} from the liquid alloy takes place. (Japanese)

Photoluminescence from Passive Oxide Films on Nickel and Chromium by Photo-excitation of UV Light

Yusuke Mito, Mikito Ueda, and Toshiaki Ohtsuka

Corrosion Science, **51**, 1540-44 (2009)

Photo-luminescence emission was measured from the thin passive oxide film on nickel and chromium under the in-situ condition in 0.1 kmol m^{-3} (M) sulfuric acid solution at pH 0.9 and neutral buffer solution of borate-boric acid mixture at pH 8.4 in order to obtain the insight of the electronic properties in the passive oxide film as thin as a few nm. The photo-luminescence induced by UV laser beam at 325 nm wavelength from nickel oxidized in both pH 0.9 sulfuric acid and pH 8.4 borate buffer solutions exhibited a broad spectrum feature with a peak at 400-420nm. The energy of the peak wavelength from 400 to 420nm is 2.95-3.10eV which may correspond to the bandgap energy of the semiconduncting NiO. The photo-luminescence spectra from chromium oxidized in the sulfuric acid and neutral borate solutions had a peak at 400 nm and about 440 nm, respectively. This photo-emission from nickel and chromium oxidized is assumed to correspond to luminescence accompanied by recombination between excess electrons produced by UV light illumination in the conduction band and positive holes in the valence band. The broad tailing of the luminescence at longer wavelength side may represent high density of localized states originated in an amorphous nature of the passive oxides.

Effect of Oxide Film on Oxygen Reduction Current for The Platinum-cobalt Alloy Electrode in PEFC

Yuichi Tamura, Kento Taneda, Mikito Ueda, Toshiaki Ohtsuka

Corrosion Science, **51**, 1560-64 (2009)

Effect of surface oxide on Pt-Co alloy electrodes on the oxygen reduction reaction (ORR) was investigated in 0.5 M sulfuric acid solution by electrochemistry, ellipsometry, laser Raman scattering spectroscopy, and XPS. The oxide as thick as 1-2 nm increases the overpotential of ORR and falls down efficiency of PEFC. The thickness of the oxide films is precisely determined by ellipsometry. The oxide film 1.9 nm thick was formed on Pt-50 *mol* % Co electrode by constant potential oxidation at 1.20 V and the film 1.5 nm thick remains on the electrode at 0.6 V at which ORR already starts. The remaining oxide decreases the current density of ORR and increases the overpotential. On pure platinum electrode, the similar influence of the oxide film was observed.

Depth Profile Analysis of Thin Passive Films on Stainless Steel by Glow Discharge Optical Emission Spectroscopy

M. Uemura, T. Yamamoto, K. Fushimi, Y. Aoki, K. Shimizu, H. Habazaki

Corrosion Science, **51**, 1554-1559 (2009)

Thin passive films formed on highly corrosion-resistant type-312L stainless steel, containing 20 mass% chromium and 6 mass% molybdenum, in 2 mol dm^{-3} HCl solution at 293 K have been analyzed by glow discharge optical emission spectroscopy (GDOES). The stainless steel does not suffer pitting corrosion even in this aggressive solution, showing a wide passive potential region. The depth profiles obtained clearly show a two-layer structure of the air-formed and passive films: an outer iron-rich layer and an inner layer highly enriched in chromium. Alloy-constituting molybdenum is deficient in the inner layer of the passive films and is enriched in the outer layer, particularly at the active dissolution potential. The molybdenum species in the outer layer may retard the active dissolution of stainless steel, promoting the formation of stable passive films highly enriched in chromium. Chloride ions are present only at the outermost part of the passive films, not penetrating into the interior part.

Formation of Porous Niobium Films by Oblique Angle Deposition: Influence of Substrate Morphology

M. Tauseef Tanvir, Y. Aoki and H. Habazaki

Thin Solid Films, **517**, 6711-6716 (2009)

The present work demonstrates the formation of porous niobium films with separated columnar structures by oblique angle magnetron sputtering for capacitor application. The niobium films deposited on textured aluminium substrates, which had concave cell structures with the cell sizes ranging from 125 nm to 550 nm, consist of isolated columns of niobium with wider gaps between columns developing on the substrates with larger cell sizes. The surface areas of the deposited films, evaluated by the capacitance of the anodic films formed at several voltages, increased with an increase in the cell size of substrate. The surface area decreases with an increase in the formation potential of anodic films from 2 V to 10 V vs Ag/AgCl, because the gaps are filled with anodic oxide as a consequence of the large Pilling–Bedworth ratio of 2.6 for the Nb/Nb_2O_5 system. The reduction of the surface area is suppressed when the substrate with larger cell size is used, due to the formation of niobium columns with wider gaps, which are not filled with anodic oxide. The high surface area even at higher formation voltages of the anodic films is a requisite for capacitor application.

Improved Electrical Properties of Silicon-incorporated Anodic Niobium Oxide Formed on Porous Nb-Si Substrate

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

Applied Surface Science, **255**, 8383-8389 (2009)

In the present study, porous Nb–Si alloy films with isolated nano-column morphology have been successfully developed by oblique angle magnetron sputtering on to aluminum substrate with concave cell structure. The deposited films are amorphous with the 15 at% silicon supersaturated into niobium. The porous Nb-15 at% Si films, as well as niobium films with similar morphology, are anodized at several voltages up to 50 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte. Due to the presence of sufficient gaps between neighboring columns, the gaps are not filled with anodic oxide, despite the large Pilling–Bedworth ratio (for instance, 2.6 for Nb/Nb_2O_5) and hence, a linear correlation between the reciprocal of capacitance and formation voltage is obtained for the Nb-15 at% Si. From the comparison with the anodic films formed on porous niobium films, it has been found that silicon addition improves the thermal stability of anodic niobium oxide; the change in capacitance and increase in leakage current become small for the Nb–Si. The findings indicate the potential of oblique angle deposition to tailor porous non-equilibrium niobium alloy films for high performance niobium-base capacitor.

Anodic Behavior of Nickel in Acidic Perchlorate Solution Containing Pb^{2+}

M. Seo, N. Kikuchi, K. Fushimi, H. Habazaki, T. Narita and T. Nakayama

ECS Transactions, **16**, 109-116 (2009)

The anodic behavior of nickel has been investigated in deaerated acidic perchlorate solution containing 10^{-4} M Pb^{2+} at room temperature. The addition of Pb^{2+} in solution shifted the corrosion potential or the potential of anodic current peak to the more noble direction and suppressed the anodic dissolution of nickel. The Tafel slope of anodic dissolution decreased from 37 mV decade^{-1} to 13 mV decade^{-1} due to the addition of Pb^{2+}. The uderpotential deposition (UPD) of Pb on nickel was discussed with relation to the effect of Pb^{2+} on anodic behavior of nickel.

Effect of Sulfuric Acid on Pit Propagation Behaviour of Aluminium under AC Etch Process

S. Ono and H. Habazaki

Corrosion Science, **51**, 2364-2370 (2009)

Pit propagation on high purity aluminium electrode in 2M HCl solutions with and without H_2SO_4 under an alternating current (AC) has been examined. Pit development and potential transients were dependent on the H_2SO_4 concentration. In the sulfate-free etchant, most pits developed from the pretreated surface, with little tendency to form clusters of pits. With increasing H_2SO_4 concentration the size of the pit clusters increased. There is an optimal H_2SO_4 concentration, which is 0.01M H_2SO_4 in this study, to form a deep etched layer of uniform thickness with high surface area. At H_2SO_4 concentrations higher than 0.01M, the pit propagation proceeded on limited foil surface sites and deep etched regions were formed locally, since sulfate ions assisted passivation and reduced the number of pit nucleation sites on foil surface. Analysis of potential transients during the anodic half-cycle supports the hypothesis that sulfate ions retarded the pit nucleation.

Preparation of Self-organized Porous Anodic Niobium Oxide Microcones and Their Surface Wettability

Y. Oikawa, T. Minami, H. Mayama, K. Tsujii, K. Fushimi, Y. Aoki, P. Skeldon, G. E. Thompson, H. Habazaki

Acta Materialia, **57**, 3941-3946 (2009)

Porous anodic niobium oxide with a pore size of ~10 nm was formed at 10 V in glycerol electrolyte containing 0.6 mol dm^{-3} K_2HPO_4 and 0.2 mol dm^{-3} K_3PO_4 at 433 K. After prolonged anodizing for 5.4 ks, niobium oxide microcones develop on the surface. X-ray diffraction patterns of the anodized specimens revealed that the initially formed anodic oxide is amorphous, but an amorphous-to-crystalline transition occurs during anodizing. As a consequence of the preferential chemical dissolution of the initially formed amorphous oxide, due to different solubility of the amorphous and crystalline oxides, crystalline oxide microcones appear on the film surface after prolonged anodizing. The surface is superhydrophilic. After coating with fluorinated alkylsilane, the surface becomes superhydrophobic with a contact angle of 158° for water. The surface is also oil repellent, with a contact angle as high as 140° for salad oil.

Spark Anodizing Behaviour of Titanium and Its Alloys in Alkaline Aluminate Electrolyte

M. Nakajima, Y. Miura, K. Fushimi and H. Habazaki

Corrosion Science, **51**, 1534-1539 (2009)

Spark anodizing of titanium, Ti-6Al-4V and Ti-15V-3Al-3Cr-3Sn in alkaline aluminate electrolyte produces highly crystalline anodic films consisting mainly of Al_2TiO_5 with α- and γ-Al_2O_3 as minor oxide phases, irrespective of substrate composition. However, the apparent efficiency for film formation decreases in the following order: Ti-6Al-4V, titanium and Ti-15V-3Al-3Cr-3Sn. A large amount of aluminium species are incorporated from the electrolyte, probably by plasma-chemical reaction, and become distributed throughout the film thickness. This distribution indicates that the electrolyte penetrates near to the film/substrate interface through the discharge channels. Thus, the outwardly migrating aluminium ions under a high electric field can be present even in the inner part of the anodic films. Voids are developed at the film/substrate interface, particularly on the vanadium-containing alloys, reducing the adhesion of the anodic film to the substrate.

The Influence of Thermal Treatment on The Electronic Properties of a-Nb_2O_5

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

ECS Transactions, **19**, 411-422 (2009)

The effect of thermal treatment for 1h at 250°C in air or under vacuum on the electronic structure of thick amorphous anodic niobia was characterized by electrochemical impedance, differential admittance (DA) and photocurrent spectroscopy (PCS). The analysis of anodized niobia has revealed that it behaves as a pure dielectric. The thermal treatment in air increases the value of its differential capacitance. The effect is stronger when the thermal treatment is carried out in vacuum, and can be cancelled by reanodizing the oxide to its initial formation potential. The frequency dependence of the sample treated in vacuum exhibited behavior typical of a semiconducting amorphous material. PCS measurements were used to derive the optical band gap value and to confirm the location of the flat band potential that was derived from admittance data.

Characterization of Amorphous Anodic Nb_2O_5 Nanofilm for Gas Sensing

D. Kowalski, Y. Aoki, H. Habazaki

ECS Transactions, **16**, 57-65 (2009)

Amorphous Nb_2O_5 film of 167 nm thickness was fabricated by anodic oxidn. of sputter deposited niobium and characterized by TEM, GD-OES and AFM. The electric properties of the anodic films with sputter-deposited circular gold electrodes were studied by AC impedance spectroscopy in ambient gas atmospheres of air, argon, oxygen or hydrogen in the temp. range of 25 - 200°C. The amorphous Nb_2O_5 showed the character of n-type semiconductor. The cond. of the film, following the Arrhenius behavior, was independent of the oxygen partial pressure, but was largely dependent on hydrogen partial pressure. The conductivity of the Nb_2O_5 film at room temperature in dry hydrogen was 2.2 orders of magnitude as high as that in air. The enhanced cond. could be associated with partial reduction of Nb^{5+} in dry hydrogen atmosphere. The addition of water vapor to hydrogen atm. reduced conductivity probably due to suppressing the reduction of Nb_2O_5.

High Proton Conductivity in Anodic ZrO_2/WO_3 Nanofilms

D. Kowalski, Y. Aoki and H. Habazaki

Angewandte Chemie-International Edition, **48**, 7582-7585 (2009)

Amorphous double-oxide nanofilm (ZrO_2/WO_3) is a new class of proton-conducting electrolyte that can be simply fabricated by physical vapor deposition (PVD) and anodic oxidation of Zr/W alloy film. The practical area-specific resistivity of 0.2 Ω cm^2 is reached at a temperature as low as 100 °C for a 60 nm thick oxide film.

Importance of Water Content in Formation of Porous Anodic Niobium Oxide Films in Hot Phosphate-glycerol Electrolyte

H. Habazaki, Y. Oikawa, K. Fushimi, Y. Aoki, K. Shimizu,
P. Skeldon, G. E. Thompson

Electrochimica Acta, **54**, 946-951 (2009)

Niobium has been anodized at a constant current density to 10 V with a current decay in 0.8 mol dm^{-3} K_2HPO_4-glycerol electrolyte containing 0.08-0.65 mass% water at 433 K to develop porous anodic oxide films. The film growth rate is markedly increased when the water content is reduced to 0.08 mass%; a 28 μm-thick porous film is developed in this electrolyte by anodizing for 3.6 ks, while the thickness is 4.6 and 2.6 μm in the electrolytes containing 0.16 and 0.65 mass% water respectively. For all the electrolytes, the film thickness changes approximately linearly with the charge passed during anodizing, indicating that chemical dissolution of the developing oxide is negligible. SIMS depth profiling analysis was carried for anodic films formed in electrolyte containing ~0.4 mass% water with and without enrichment of $H_2{}^{18}O$. Findings disclose that water in the electrolyte is a predominant source of oxygen in the anodic oxide films. The anodic films formed in the electrolyte containing 0.65 mass% water are practically free from phosphorus species. Reduction in water content increased the incorporation of phosphorus species.

Optimized Observation of Tungsten Tracers for Investigation of Formation of Porous Anodic Alumina

S. J. Garcia-Vergara, D. Le Clere, T. Hashimoto, H. Habazaki,
P. Skeldon, G. E. Thompson

Electrochimica Acta, **54**, 6403-6411 (2009)

Improved methods are presented for investigating the flow of anodic alumina during the formation of porous anodic films on aluminium in phosphoric acid. In particular, the use of tungsten nanolayer tracers with increased flatness is shown to result in enhanced definition of the influences of flow on the tracer distribution, as observed by electron microscopy. Additionally, taper sectioning of films, by ultramicrotomy, and parallel sectioning of films, by sputtering using an Ar^+ ion plasma, enable tungsten distributions across cells to be determined. In the case of an Al-3.5 at.% W alloy, the flow results in an inner alumina layer lining the pore walls that is relatively free of tungsten species and an outer cell layer of comparatively high tungsten content. Both sectioning procedures also show the presence of fine cell boundary bands of relatively high tungsten content, which are suggested to result from the transport of tungsten, enriched in the alloy immediately beneath the film, toward the cell boundary by the alloy/film interface.

Growth of Porous Anodic Films on Sputtering-deposited Aluminium Incorporating Al-Hf Alloy Nanolayers

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

Electrochimica Acta, **54**, 3662-3670 (2009)

Formation of porous anodic films on sputtering-deposited aluminium incorporating Al-Hf tracer layers has been examined at constant current in sulphuric and phosphoric acids. Hafnium was selected as the tracer species since the migration rates of Hf^{4+} and Al^{3+} ions are similar in barrier-type anodic alumina. The distribution of hafnium in the films was determined using ion beam analysis, scanning electron microscopy and transmission electron microscopy. Increases in the anodizing voltage and barrier layer thickness accompany the oxidation of hafnium and the migration of Hf^{4+} ions through the barrier layer region of the porous film. Hf^{4+} and Al^{3+} ions that migrate to the pore bases are lost to the electrolyte. Other Hf^{4+} ions are incorporated into the cell walls. For films formed in phosphoric acid, with relatively thick barrier layers, channelling of the ion current leads to accelerated outward transport of Hf^{4+} ions toward the pore base, while a U-shaped inner edge of the hafnium distribution beneath the pores is associated with more slowly transported hafnium species. The tracer behaviours for films formed in both acids are consistent with the transport of Hf^{4+} ions in the barrier layer regions by a combination of flow of film material and ion migration, the flow being a key factor in the development of the pores. The percentage losses of Hf^{4+} and Al^{3+} ions from the films to the electrolyte are relatively Similar, correlating with their similar migration rates, and contrast with the retention in the film of slow migrating W^{6+} ions, found previously, due to a more dominant role of flow.

Formation of Porous Aluminum Films with Isolated Columnar Structure using Physical Vapor Deposition for Medium-voltage and High-voltage Capacitors

T. Fujii, Y. Aoki, K. Fushimi, T. Makino, S. Ono, H. Habazaki

J. Surf. Finish. Soc. Jpn., **60**, 166-169 (2009)

An attempt was made to tailor porous aluminum films with an isolated columnar structure by magnetron sputtering for potential application to medium-voltage and high-voltage electrolytic capacitors. The aluminum film was deposited at a relatively high Ar pressure of 3.3 Pa on rough aluminum substrate with a cellular texture. Shadowing effects, which were enhanced by the random incident angle of aluminum atoms at the high Ar pressure and the use of a rough substrate, produced the isolated columnar structure of the deposited film. However, gaps separating neighboring columns were not high enough to maintain high surface roughness after anodic oxide formation, due to the large Pilling-Bedworth ratio for the Al/Al_2O_3 system. The gaps became filler with anodic oxide during anodic film formation. Slight alkaline etching of the deposited film the increased the gaps such that high surface area was maintained to high formation voltages.

Formation of Anodic films on Sputtering-deposited Al-Hf Alloys

M. Fogazza, M. Santamaria, F. Di Quarto, S. J. Garcia-Vergara, I. Molchan, P. Skeldon, G. E. Thompson, H. Habazaki

Electrochimica Acta, **54**, 1070-1075 (2009)

The growth of barrier-type anodic films at high efficiency on a range of sputtering-deposited Al-Hf alloys, containing from 1 to 95 at.% Hf, has been investigated in ammonium pentaborate electrolyte. The alloys encompassed nanocrystalline and amorphous structures, the latter being produced for alloys containing from 26 to 61 at.% Hf. Except at the highest hafnium content, the films were amorphous and contained units of HfO_2 and Al_2O_3 distributed relatively uniformly through the film thickness. Boron species were confined to outer regions of the films. The boron distributions suggest that the cation transport number decreases progressively with increasing hafnium concentration in the films, from ~0.4 in anodic alumina to ~0.2 for a film on an Al-61 at.% Hf alloy. The distributions of Al^{3+} and Hf^{4+} ions in the films indicate their similar migration rates, which correlates with the similarity of the energies of Al^{3+}-O^{2-} and Hf^{4+}-O^{2-} bonds. For an alloy containing ~95 at.% Hf, the film was largely nanocrystalline, with a thin layer of amorphous oxide, of non-uniform thickness, at the film surface. The formation ratios for the films on the alloys changed approximately in proportion to the hafnium content of the films between the values for anodic alumina and anodic hafnia, ~1.2 and 1.8 nm V^{-1} respectively.

Enhanced Proton Conductivity of Amorphous Silicate Nanofilms

Y. Aoki, H. Habazaki, T Kunitake

ECS Transactions, **16**, 407-412 (2009)

$Al_xSi_{1-x}O_n$ films exhibit a drastic change of proton conductivity across the film by reducing its 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.

Size-Scaling of Proton Conductivity in Amorphous Aluminosilicate Acid Thin Films

Y. Aoki, H. Habazaki and T. Kunitake

Journal of the American Chemical Society, **131**, 14399-14406 (2009)

Amorphous aluminosilicate nanofilms, a-$Al_{0.1}Si_{0.9}O_x$, exhibit unique size-enhancement of the proton conductivity along the thickness direction because of the presence of the zeolite-like, acid site network with the mesoscopically sized dimension inside glass matrix. The dense films with the thickness of 22-1400 nm were uniformly formed over the electrode substrate in nanometer thickness precision by multiple spin-coating with a mixed precursor Sol. XANES measurements indicated that the basic framework of a-$Al_{0.1}Si_{0.9}O_x$ films was similar to the zeolitic one, consisting of the corner-linkage of SiO_4 and AlO_4 tetrahedral units. These films revealed the complex temperature- and humidity-dependency of proton conductivity by the existence of two kinds of protonic carriers: Bronsted acidic protons and Lewis acidic protons. The Bronsted acidic protons could be persistent in amorphous films at around 500°C, as checked by thermal desorption spectroscopy, so that the film exhibited the humidity-independent proton conductivity at temperatures above 300°C. Furthermore, the conductivity across the film increased in a power low by reduction of the film thickness of to less than 120 nm. The observed scaling index was 2.2 in agreement with the value of the theoretical index (2.3) of cluster size scaling in a three-dimensional percolation system. This conduction behavior is explicable by finite size-scaling of the highly conductive pathway based on the interconnected Bronsted acid centers in the range of a few tens to hundreds of nanometers.

Oxide Scale Formed on Al-Mg Alloys in H_2O-Containing Atmosphere

T. Kurosaki, A. Yamauchi, K. Kurokawa

Applied Plasma Science, **17**, 73-77 (2009)

Two kinds of Al-Mg alloys are oxidized in dry and wet conditions at 773 K for 6hr. The oxidized specimens were observed and analyzed by TEM, SEM, EDS and AES to investigate the effect of Mg content and water vapor on the structures of scales formed on Al-Mg alloys by oxidation. At the all specimens, a thin oxide layer was formed after oxidation. Despite of low Mg content, the surface oxide layer composed of MgO and a sub-scale of Al_2O_3 or $MgAl_2O_4$ is also formed. The range of scale thickness was 5 – 50 nm. The thickness of oxide layer increased with Mg content. In addition, existence of water vapor also led to increase in the scale thickness. (Japanese)

The Influence of Cr Addition on the High Temperature Corrosion of CoNiCrAlY Alloys

T. Sudiro, T. Sano, A. Yamauchi, S. Taniguchi, A. Kobayashi, K. Kurokawa

Advances in Applied Plasma Science, 7, 295-298 (2009)

CoNiCrAlY alloys with 0, 10, 20, and 30 mass% Cr were prepared using a spark plasma sintering (SPS) technique. In order to clarify the influence of Cr addition on the resistance against high temperature corrosion of CoNiCrAlY alloys, the corrosion tests were carried out in Na_2SO_4 + 25mass% NaCl fused salt at the elevated temperature of 923 K, 1073 K, and 1273 K for up to 100 hr. Corrosion products in gas phase are mainly Cr_2O_3 in high Cr-CoNiCrAlY at 923 K and Al2O3 in high Cr-CoNiCrAlY at 1073 K and 1273 K. Cr addition led to degradation of the high temperature corrosion resistance of CoNiCrAlY at 923 K and at 1273 K. However, at 1073 K, Cr addition has a better corrosion resistance.

Reaction Behavior of Commercial Steels in Molten Lead-free Solders

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

15th Symposium on "Microjoining and Assembly Technology in Electronics", **15**, 399-402 (2009)

The purpose of present study is to investigate the reaction behavior of various commercial Fe-based alloys in molten lead-free solders. In low carbon steel and pure iron, these reaction behaviors are almost same. The change of thickness of IMC layer that formed between solder and substrate obeys parabolic rate law. On the other hands, the reaction behaviors of stainless steels are different. In SUS430, the reaction area with solder is uniform, and then the interface between IMC and substrate is smooth. In SUS304 and SUS316, local corrosion occurs. The morphology of interface between IMC and substrate shows kinds of pitting corrosion. In addition, SUS316 has a good corrosion resistance in the molten lead-free solder. The corrosion resistance for the molten lead-free solder depends on the maintenance of sound scale formed on substrate. (Japanese)

Formation of Microstructures of Sn-based Alloys at Minute Stress Loading

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

15th Symposium on "Microjoining and Assembly Technology in Electronics", **15**, 77-82 (2009)

The formation of sub-grain structures inside grains of β-Sn on Sn-based alloys under stress loading has been reported. In this paper, we investigated differences of sub-grain size depended on additional elements for Sn-based alloys. As a result, it was found that sub-grains of Al or Bi added specimens are very fine compared to that of pure Sn. However, the effect of Al addition dissolved on Cu contained alloys. (Japanese)

Corrosion Behavior of Fe-based Alloys with Additional Elements in Molten Lead-free Solders

T. Kawamoto, A. Yamauchi, S. Kawakubo, A. Irisawa, K. Kurokawa, J. Tanaka

19th Symposium of Micro Electronics, **19**, 73-76 (2009)

The purpose of this study is to investigate the effects of additional elements on the corrosion behavior of Fe-based alloys and low carbon steel in the molten lead-free solders. It is clear that the addition of chromium and titanium to the low carbon steel improves the thickness of consumed substrate. On the other hand, the addition of molybdenum for the improvement of thickness of consumed substrate was not found. Moreover, the reaction layers that were formed on Fe-based alloys were consisted of iron and tin intermetallic compounds ($FeSn_2$). (Japanese)

Effect of Composition on Microstructure of Sn-Ag Solders

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

19th Symposium of Micro Electronics, **19**, 77-80 (2009)

The effect of the composition and the cooling rate on the microstructure of Sn-Ag and Sn-Ag-Cu solders has not been well investigated in detail. The purpose of this study is to investigate the effect of composition and the cooling rate on the microstructures of the Sn-Ag and Sn-Ag-Cu solders. From the observation of microstructures showed that the secondary phase that consisting of Sn and Ag3Sn precipitated in Sn-Ag-Cu solders and their growth was observed. This coarsening Ag3Sn affects the mechanical property of the solder. Thus, the microstructure becomes complicated due to the change of the phase ratio. (Japanese)

Biointeractive and Bioreactive Nature of Nanomaterials

Fumio WATARI

Nano Biomedicine, **1**, 2-8 (2009)

Biological reactions of nano/micro materials are discussed. Nanomaterials are biointeractive in the sense that their size and existence themselves possess the nature to induce the bioreaction to cells and tissue. They are also bioreactive, since they induce the intrinsic functions of biological organism in a generalized sense of both merit (bioactive) and demerit (toxic) for human beings. The bilateral nature of the potentiality for both high functional performance (nanotechnology) and unintentionally occurring biohazard (nanotoxicology) is the essential properties of nano/ micro materials.

Analysis of Wear Debris Generated from the Metal-on-metal Hip Joint

M.Uo, F.Watari, K.Asakura, N.Katayama, S.Onodera, H.Tohyama,
K.Hamada, S.Ohnuki

Nano Biomedicine, **1**, 133-136 (2009)

The elemental concentration, shape and chemical state of debris contained in the articular capsules of metal-on-metal hip joints were examined. Co derived from Co-Cr alloy was detected with high concentration. By TEM observation, some larger debris in several hundred nanometers and a lot of smaller debris smaller than several ten nanometers were observed. The debris could be observed in the severe metallosis region. Most of Co contained in the articular capsules could be estimated as the metallic state by fluorescence XAFS analysis, which provides high sensitivity for chemical state analysis. Therefore, the metallosis of the articular capsule could be assumed as mainly caused by the metallic debris.

Capture of Bacteria by Flexible Carbon Nanotubes

T.Akasaka, F.Watari

Acta Biomaterialia, **5**, 607-612 (2009)

Capture of bacteria with flexible carbon nanotubes (CNTs) was done in vitro. Bundles of single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) was mixed with *Streptococcus mutans*. Precipitation assays and colonyforming unit formation assays showed free *S. mutans* in the solution was significantly decreased by the addition of the CNTs. Observation of the precipitate by scanning electron microscopy showed bacterial adhesion to CNTs. It has been shown that CNTs of different diameters have significantly different effects on the precipitation efficiency, and the manners in which they capture the cells are different. We found that MWCNTs (diameter of approximately 30 nm) had the highest precipitation efficiency, which was attributable to both their adequate dispersibility and aggregation activity. From observations by scanning electron microscopy, bundles of SWCNTs and thin MWCNTs (diameter of approximately 30 nm), which were moderately flexible, were easily wound around the curved surface of *S. mutans*. Bare CNTs having high adhesive ability could be useful as biomaterials, e.g., as tools for the elimination of oral pathogens at the nano-level.

Adhesion of Human Osteoblast-like Cells (Saos-2) to Carbon Nanotube Sheets

T.Akasaka, A.Yokoyama, M.Matsuoka, T.Hashimoto, S.Abe, M.Uo and F.Watari

Bio-Medical Materials and Engineering, 19, 147-153 (2009)

Carbon nanotubes (CNTs) exhibit excellent cell proliferation properties, which can serve as a scaffold for cell culturing. However, there are only a few reports on adhesion of osteoblast-like cells to a CNT sheet. In this study, we investigated adhesion of osteoblast-like cells to single-walled carbon nanotube (SWNT) and multi-walled carbon nanotube (MWNT) sheets and compared these adhesions with that on a cell culture polystyrene dish by using a cell adhesion test and a scanning electron microscope. The MWNT sheets exhibited faster adhesion of cells at an initial stage than SWNT sheets and cell culture polystyrene dish. The number of attached cells on theMWNT sheets seemed to be greater than on SWNT sheets and cell culture polystyrene. Moreover, the MWNT sheets exhibited both high speed and good capacity for cell adhesion. However, the surface of the MWNT sheets was such that it facilitated cell adherence but hindered the spreading of the attached cells. Interestingly, cell adhesion to CNT sheets was significantly influenced by pre-coating with serum. These results indicate that CNT sheets would play an important role in adsorption of serum proteins, which would consequently facilitate cell adhesion, and that the MWNT sheets have a high cell adhesiveness.

Modification of the Dentin Surface by using Carbon Nanotubes

T.Akasaka, K.Nakata, M.Uo, F.Watari

Bio-Medical Materials and Engineering, **19**, 179-185 (2009)

Recent studies have shown that carbon nanotubes (CNTs) can be used as biomedical materials because of their unique properties. CNTs effect nucleation of hydroxyapatite, because of which considerable interest has been generated regarding the use of CNTs in dentistry. However, there are only a few reports on the use of CNTs as dental materials. In this study, we investigated the changes induced in the surfaces of tooth slices by the application of a coating of CNTs by observing CNTcoated tooth slices both macroscopically as well as under a scanning electron microscope. Further, we investigated the effect of CNT coating on the tensile bond strength of dentin adhesives. CNTs adhered easily to the tooth surfaces when tooth slices were suspended in a CNT-dispersed solution. Interestingly, it was observed that CNTs selectively adhered to the surfaces of dentin and cementum, possibly by adhering to their exposed collagen fibers. In addition, the CNT coating did not affect the tensile bond strength of dentin adhesives. These results indicate that coating of the teeth with CNTs can be a possible application of CNTs as dental materials.

Time-dependence and Visualization of TiO_2 and Pt Particle Biodistribution in Mice

S.Abe, C.Koyama, M.Uo, T.Akasaka, Y.Kuboki, F.Watari

J. Nanoscience Nanotechnology, **9**, 4988-4991, (2009)

Micro- and nano-sized materials have received much attention regarding their biocompatibility and toxicity. To understand the influence of such materials on animals, it is very important to determine their internal distribution behavior. In this study, the biodistributions of Pt and TiO_2 micro- and nano-sized particles in mice were estimated and visualized by X-ray scanning analytical microscopy and inductively coupled plasma-atomic emission spectroscopy. We also determined the effect of particle size, difference between metal and oxide, and time dependence for the distributions, because the biodistribution depends upon both the chemical character of materials and the size of particles. The results of the present study indicated that the difference in chemical character had a greater effect than did particle size. We predict that X-ray scanning analytical microscopy will be a useful method for studying biodistribution of micro- and nano-sized particles, because this method requires no labeling or treatment of the target particles.

Internal Distribution of Several Inorganic Microparticles in Mice

S.Abe, C.Koyama, T. Akasaka, M.Uo, Y.Kuboki, and F.Watari

Key Engineering Materials, 396-398, 539-542 (2009)

We observed the internal diffusion behavior of inorganic micro/nano particles through oral administration. By oral exposure, the fed particles were absorbed through the digestive system then reached some organs after internal diffusion in the body. For example, TiO_2 particles fed to mice were detected in the lung, liver, and spleen after 10 days of feeding. Whereas, the absorption efficiency was extremely low compared with intravenous injection. In a comparison of the simple amount of administration, oral exposure required 10^2 times or more amount by intravenous injection for detection by an X-ray scanning analytical microscope. During dental treatment, micro/nano particles from tooth or dental materials would generate in the oral cavity, and some of the particles had a possibility to be swallowed, absorbed through the digestive system, and then diffuse into the body. However, our results suggest that biocompatible microparticles that are naturally taken orally affect animals only rarely because of the low absorption efficiency.

A DFT and MD Study on the Interaction of Carbon Nano-materials with Metal Ions

S.Abe, F.Watari, T.Takada, H.Tachikawa

Molecular Crystals and Liquid Crystals, **505**, 289-296 (2009)

The interaction of manganese (II) ion (Mn^{2+}) with graphene surfaces have been investigated by means of density functional theory (DFT). Also, the molecular dynamics (MD) calculations using molecular mechanics-2 (MM2) potential functions have been applied to the diffusion dynamics of Mn^{2+} on the graphene surface. Two graphene sheets (*n*= 19 and 52, where *n* means numbers of rings in each carbon cluster) were considered as models of graphene surface in the present study. The B3LYP/LANL2MB calculations showed that the Mn^{2+} ion is located in the ranges 2.28-2.46 Å from the graphene surface. Also, classical MD calculation was applied to diffusion processes of the Mn^{2+} on the graphene surface (*n*= 52). The classical MD calculations showed that the Mn^{2+} ion diffuses from bulk to edge region at 300-600 K and is trapped in the edge region. The nature of the interaction between the Mn^{2+} ion and the graphene sheet was discussed on the basis of theoretical results.

Controlled Calcification using Polyanionic Macromolecules with an Active Reaction Center Analogue of *Carbonic Anhydrase*

S.Abe, T.Ishida, E.Yamatoya, D.Hayashi, T.Akasaka, M.Uo,
F.Watari, T. Takada

Nano Biomedicine, **1**, 51-58 (2009)

Biomimetic macromolecules containing carboxyl and imidazole groups were synthesized. The complex of a zinc ion, a water molecule, and three imidazoles in a polymer is expected to act as an active center analogue of carbonic anhydrase, a hydration enzyme. The obtained polymer complex was applied to calcium carbonate formation. In this study, we investigated the role of both functional groups on the calcification reaction. The presence of a carboxyl group drastically enhanced the biomineralization, because it recognized and condensed the calcium ion at the first step of the calcification reaction. The obtained zinc-imidazole complex selectively induced the formation of vaterite, which is well-known to be a thermodynamically metastable polymorph of calcium carbonate. Interestingly, the results suggest that the active center analogue (zinc-imidazole complex) also stimulates introduction of the HCO_3^- ion to the calcium ion recognition site.

Observation of Biodistribution of Indium-Tin Oxide Nanoparticles in Mice

S.Abe, T.Yonezawa, T.Akasaka, M.Uo, F.Uchida, F.Watari

Nano Biomedicine, **1**, 70-74 (2009)

We have observed biodistribution of tin-doped indium oxide nanoparticles with the size of ca. 10 nm. After the particles administered into mice through the tail vein, the organs were excited at several post-injection time then the specimens were subjected with X-ray scanning analytical microscope. The obtained fluorescent X-ray images of indium element clearly indicated that the injected nanoparticles reached and condensed temporally in the lung, liver, and spleen (especially, lung). The distributions among the organs were changed by the post-injection time. The amount of nanoparticles in organs rapidly decreases within 4 weeks.

Biodistribution Imaging of Magnetic Nanoparticles in Mice Compared with X-ray Scanning Analytical Microscopy and Magnetic Resonance Imaging

S.Abe, I.Kida, M.Esaki, T.Akasaka, M.Uo, Y.Sato, B.Jeyadevan, Y.Kuboki,
M.Morita, K.Tohji, F.Watari

Bio-Medical Materials and Engineering, **19**, 213-220 (2009)

Nano-sized particles have received much attention in view of their varied application in a wide range of fields. For example, magnetite (Fe_3O_4) nanoparticles have been investigated for various medical applications. In this study, we visualized the distribution of administered magnetic nanoparticles in mice using both X-ray scanning analytical microscopy (XSAM) and magnetic resonance imaging (MRI). After administration, the nanoparticles were rapidly dispersed via the blood circulation, and reached the liver, kidney and spleen. Using the XSAM and MRI methods in a complementary fashion, the biodistribution of nano-sized magnetite particles was successfully visualized.

In vivo Internal Diffusion of Several Inorganic Microparticles Through an Oral Administration

S.Abe, C.Koyama, M.Esaki, T.Akasaka, M.Uo, Y.Kuboki, M.Morita, F.Watari

Bio-Medical Materials and Engineering, **19**, 221-229 (2009)

We observed the internal diffusion behavior of inorganic micro/nano particles through oral administration. By oral exposure, the fed particles were absorbed through the digestive system then reached some organs after internal diffusion in the body. For example, TiO_2 particles fed to mice were detected in the lung, liver, and spleen after 10 days of feeding. Whereas, the absorption efficiency was extremely low compared with intravenous injection. In a comparison of the simple amount of administration, oral exposure required 10^2 times or more amount by intravenous injection for detection by an X-ray scanning analytical microscope. During dental treatment, micro/nano particles from tooth or dental materials would generate in the oral cavity, and some of the particles had a possibility to be swallowed, absorbed through the digestive system, and then diffuse into the body. However, our results suggest that biocompatible microparticles that are naturally taken orally affect animals only rarely because of the low absorption efficiency.

Synthesis and Characterization of a Water Aoluble Multi-walled Carbon Nanotube and Its Biodistribution in Mice

S.Abe, D.Hayashi, T.Akasaka, M.Uo, Y.Kuboki, F.Watari, and T.Takada

Nano Biomedicine, **1**, 143-150 (2009)

In this study, we have succeeded in synthesizing and characterizing a water-soluble multi-walled carbon nanotube. Nanotubes have been functionalized with many hydrophilic carboxylic groups on the surface (3-10 wt%) by a poly-carboxylation reaction and the obtained products show stable aqueous dispersion. To examine the nanotube's preliminary biocompatibility, we injected the functionalized carbon nanotube solution into mice through the tail vein. The time-profile of the subjects' body weight had a similar tendency to that of mise in a control group during 4-week post-injection examination. The injected carbon nanotube derivatives were observed in specimens of the lung and liver using a transmission electron microscope. These results suggest that the injected carbon nanotubes reach some organs through blood circulation after injection but they did not cause serious acute toxicity in mice.

Development of a 3D Collagen Scaffold Coated With Multiwalled Carbon Nanotubes

E.Hirata, M.Uo, H.Takita, T.Akasaka, F.Watari, A.Yokoyama

Journal of Biomedical Materials Research Part B, **90B**, 629–634 (2009)

Carbon nanotubes (CNTs) have attractive biochemical properties such as strongcell adhesion and protein absorption, which are very useful for a cell cultivation scaffold. Inthis study, we prepared a multiwalled carbon nanotube-coated collagen sponge (MWCNTcoatedsponge) to improve the surface properties of the collagen sponge, and its cell culturingproperties were examined. The suface of the collagen sponge was homogeneously coated withMWCNTs by dispersion. MC3T3-E1 cells were cultured on and inside the MWCNT-coatedsponge. The DNA content on the MWCNT-coated sponge after 1 week of culture was significantly higher than on an uncoated collagen sponge ($p < 0.05$). There was no significantdifference between the estimated ALP activity normalized by DNA quantity on the MWCNTcoatedsponge and that on the uncoated collagen sponge which is well known as one of the bestscaffolds for cell cultivation. In addition, the MWCNT-coated surface shows strong celladhesion. Therefore, the MWCNT-coated collagen sponge is expected to be a useful 3Dscaffold for cell cultivation.

Improvement in Cell Proliferation on Silicone Rubber by Carbon Nanotube Coating

M. Matsuoka, T. Akasaka, T. Hashimoto, Y. Totsuka, F. Watari

Bio-Medical Materials and Engineering, **19**, 155–162 (2009)

Silicone rubbers are widely used as tissue implants because of their flexibility and chemical stability. However, they have limited cellular adhesiveness and may cause problems in the long term. In this study, a coating of carbon nanotubes (CNTs) was applied to silicone rubber to improve its cellular adhesiveness. Scanning electron micrograph of this coating revealed that CNTs had formed a densely packed meshwork; the Ra values and protein adsorption capacity were enhanced. Although the contact angle did not change after coating, it decreased after immersion into a culture medium. After cultivation for 6 d, while Saos-2 cells were hardly observed on untreated silicone, the cells proliferated on CNT-coated silicone. Thus, CNT coating might be a simple and effective solution to problems associated with silicone implants.

Culturing Osteoblast-like Cells on a Carbon Nanotube-coated Dish

M. Matsuoka, T. Akasaka, T. Hashimoto, Y. Totsuka, F. Watari

Nano Biomedicine, **1**, 17-25 (2009)

The aim of this study was to investigate the influence of CNTs on cells by culturing them in direct contact with CNTs. First, human osteoblast-like cells, Saos-2 cells, were cultured on a CNT-coated culture dish and the cell morphology, viability, adhesion, and alkaline phosphatase (ALP) activity of these cells were compared to those cultured on a culture dish. Next, Saos-2 cells cultured on each dish were subcultured onto culture dish, and the cell morphology and the ALP activity were examined. The Saos-2 cells cultured on the CNTs showed a high viability that was similar to that of the cells on culture dish. Cell adhesion test showed strong adhesiveness of the cells to multi-walled carbon nanotubes (MWCNTs) and morphological observation revealed many filopodia extending to MWCNTs. After the subculture, this morphological change disappeared. These results suggest that the Saos-2 cells a have high adhesiveness toward CNTs, especially towards MWCNTs. Moreover, the morphological change in the cells cultured on MWCNTs implies that CNTs did not induce denaturation of the cells.

Effect of Crosslinking Agent in Nanohydroxyapatite-collagen Composite on Ectopic Bone Formation with BMP-2 Application

T.Tenkumo, T.Sugaya, M.Kawanami, M.Gelinsky, F.Watari

Nano Biomedicine, **1**, 26-33 (2009)

Histological investigations of the nanohydroxyapatite-collagen composite (nHAC) foil in tissue were carried out to evaluate its possible suitability as a BMP-2 carrier for regeneration of periodontal tissue. The nanohydroxyapatite -collagen composite and its thin foil could be successfully fabricated with the crosslinking agent of either 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) or ascorbic acid / copper chloride (AA/CC). They were implanted into the subcutaneous tissue and tight muscle with and without BMP-2 for 1 and 2 weeks after surgery. nHAC was degraded and the inflammation in the surrounding area was decreased with time. nHAC(AA/CC) was degraded earlier and showed a better biocompatibility than nHAC(EDC). In the case of BMP-2 application, the different crosslinking agent showed an inverse effect. New bone formation was observed only in muscle for EDC and only in subcutaneous tissue for AA/CC. The Present results suggested that the nHAC is suitable as the carrier of BMP-2 with either the crosslinking agent of EDC or ascorbic acid / copper chloride, and the suitable crosslinking agent should be selected depending on desired conditions.

In Situ Observation of Dynamic Behavior of Liver Cells to Carbon Nanotubes and Analysis of Cell Functions

S.Itoh, T.Taira, Y.Yawaka, F.Watari

Nano Biomedicine, **1**, 95-108 (2009)

Carbon nanotubes (CNTs) are one of the most representative nanomaterials that have newly appeared and drawn much attention for various applications. To examine the effect of CNTs on biological organisms, the reaction behavior of human hepatocytes, Hc cells, to CNTs was investigated in comparison with phagocytes. After hepatocytes were incubated in the culture medium with the addition of CNTs, CNTs were found in cytoplasms by OM (Optical Microscopy), SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy). In the successive observation using the time-lapse OM system, hepatocytes showed the phagocytosis-like behavior to CNTs by changing their shapes and forming the long, straight pseudo-pods. The quantitative analysis showed that cell activities to scavenge CNT debris were constant during the observation for more than 22 hrs. Since these behaviors of hepatocytes apparently resemble those of phagocytes, the cell functional analysis was done and compared by measuring the expression of cytokines and superoxide dismutase (SOD) activity. When incubated with CNTs, THP-1 monocytes released TNF-α in a dose dependent manner to CNT content, while the amount released from hepatocytes were very low and there was almost no difference from control. These results indicate that hepatocytes have the phagocytosis-like ability to uptake foreign objects. However, their mechanism is completely different from that of phagocytotic cells in the point that they have no functions to lead to inflammation through cytokine cascade as monocytes exhibit. Throughout the study, hepatocytes could work without the acute toxicity such as cell death by CNTs. In situ observation could image the dynamic behavior of hepatocytes to perform the functions to treat the foreign objects. The results confirm that liver is an important organ to deal with them under non-inflammatory circumstances.

Physical Properties of Aluminosilicate Nanotubes, Imogolite, as Scaffold and Effect on Osteoblastic Mineralization

K.Ishikawa, T.Akasaka, Y.Nodasaka, N.Ushijima, M.Kaga, S.Abe, M.Uo,
Y.Yawaka, M.Suzuki, F.Watari

Nano Biomedicine, **1**, 109-120 (2009)

Imogolite is a naturally occurring aluminosilicate clay mineral with a nanotube structure of 2 nm in diameter and 60 nm^{-2} mm in length. In this study, synthetic imogolite nanotubes were used to fabricate a scaffold for cell culture and the properties of the resulting scaffold were compared with those of a conventional culture dish and a carbon nanotube (CNT) scaffold. The surface characteristics of the imogolite scaffold were drastically changed depending on the amount of imogolite on the dish. With the increase of imogolite concentration, the surface morphology of scaffolds changed from an island-like shape in random orientation to a self-organized fiber texture aligned in the same direction, and finally full coverage in a random orientation with plural layers. Osteoblast-like cells (Saos-2) cultured on imogolite showed a flat-form morphology developed in all directions in contrast to a spindle-shaped morphology developed in one direction on cell culture dishes (Cntl) and carbon nanotube scaffolds (CNT). The large growth of the cells proliferated on imogolite limited the smaller number of cells than the Cntl and CNT. However, the amount of normalized protein per cell on imogolite showed the value more than twice of that on Cntl. Imogolite contributed more to the enlargement of cell volume than proliferation. The cells cultured on the imogolite scaffold become more strongly bound to the substrate and showed high osteoblas-tic mineralization than those cultured on Cntl and CNT. The results indicate the good biocompatibility between cells and the imogolite scaffold, and suggest that imogolite could be useful for various bioapplications, such as for the fabrication of scaffolds for cell cultures, some useful proteins production (i.e. antibody, enzyme) and surface modified implants.

Surface Modification of Carbon Nanotubes with Calcifying Solutions for Biomedical Applications

T.Koshikawa, Y.Kuboki, M.Uo, F.Watari

Nano Biomedicine, **1,** 121-132 (2009)

In order to improve bio compatibility and biological function of carbon nanotubes (CNTs), the surface of CNTs was modified by precipitating calcium phosphate compounds in a calcifying solution. To accelerate calcification process and efficacy of modification, a solution containing 6-times higher concentration of calcium and phosphate ions than that of physiological body fluid was used (the 6-times solution). Precipitation of calcium phosphate (Ca-P) upon CNTs was investigated, concerning the incubation time, influence of concentration of CNTs, elemental analyses of products and protein adsorption on the chromatographic column. Time-dependent observation of the reaction products by SEM indicates that the moss-like precipitation of Ca-P at first, then the granular bodies appeared at the beginning of incubation. These moss-like bodies seemed to be replaced gradually by granular bodies, and later, cotton fiber shaped structures appeared. After 24 hr of incubation, the aggregation of spheroid bodies, composed of hydroxyapatite and CNTs, became the dominant constitute of the products. Ca and P were detected by EDS even when there were no precipitations in SEM image, giving the evidence that the surface CNTs was slightly covered by calcium and phosphate compounds from very early stage. This was further strengthened by a chromatographic result that the chromatography of slightly modified CNTs clearly showed the greater affinity for an acidic protein (albumin) than the unmodified CNT column. Combining with the evidence by EDS for Ca and P contents, this chromatographic result clearly indicates that the presence of calcium phosphates on the surface of CNTs, even though the observation by SEM could not detect it. The improvement of biocompatibility and the functionalization of CNTs could be done using calcification solution and the possible applications were suggested for the adsorption and release of various growth factors and medicines.

Preparation and Properties of Thermoplastic-resin-based Nanocomposites for the Development of Esthetic Orthodontic Wires

S.Yamagata, T.Akasaka, M.Uo, N.Ushijima, Y.Nodasaka, J.Iida, F.Watari

Nano Biomedicine, **1**, 151-158 (2009)

Transparent PMMA/layered silicate nanocomposites were fabricated by a solution intercalation method. Montmorillonite (MMT), organically modified with alkylammonium ions, was selected as the filler for reinforcement. Platelets of organically modified MMT were well-dispersed macro-scopically in dissolved PMMA. X-ray diffraction patterns showed that a peak regarded as a basal spacing was shifted toward the lower 2θ values, indicating a diffusion of PMMA polymer chains into interlayer regions of MMT. TEM micrographs revealed well-intercalated and partially exfoli-ated structures of organically modified MMT. Board-shaped specimens used for flexural tests were fabricated by compression molding at 230°C. The specimens were transparent enough for their use as esthetic orthodontic wires. The flexural modulus of the nanocomposites increased marginally, relative to that of PMMA, with the increasing amount of clay.

Early-Stage Oxidation Behavior of Pt-Modified γ'-Ni_3Al-Based Alloys with and without Hf Addition

S. Hayashi, B. Gleeson

Oxidation of Metals, **71**, 5-19, (2009)

The early-stage oxidation behavior in air of Pt-modified γ'-Ni_3Al-based alloys of composition (in at.%) Ni–22Al–30Pt with and without 0.5Hf was investigated in terms of oxidation kinetics, scale evolution and Al_2O_3 phase transformation. Oxidation exposures included heating to and short-term holds at 1150°C. Hafnium addition did not appear to affect microstructural evolution and growth rate of the oxide scales during heating to 1150°C; however, it was found that Hf delayed the metastable-to-α-Al_2O_3 phase transformation, thus allowing continued fast growth of oxide scale. After the transient oxidation stage of up to about 10 min (including heating time), Ni-rich metallic particles precipitated in the lower part of the metastable Al_2O_3 layer, due to a decrease in the oxygen potential resulting from scale evolution. The present results indicated that the period of oxide phase transformation was followed by the establishment of steady-state oxidation kinetics. However, the steady-state kinetics were different for the two alloy systems. Specifically, after complete phase transformation to α-Al_2O_3, rapid growth of oxide grains occurred on the Hf-free alloy; whereas, the oxide grain size remained small for the Hf-containing alloy. Such a difference of transformation and subsequent grain-growth behavior greatly affected oxide thickening kinetics.

Compositional Factors Affecting the Establishment and Maintenance of Al_2O_3 Scales on Ni-Al-Pt Systems

B. Gleeson, N. Mu, S. Hayashi

J. Mater., Sci., **44**, 1704-1710, (2009)

The beneficial role played by platinum addition in promoting the formation of a protective Al_2O_3 scale on representative γ'-Ni_3Al+γ-Ni coating compositions during high-temperature oxidation is discussed. This beneficial effect can be primarily ascribed to the fact that Pt is nonreactive, and its addition decreases the chemical activity of aluminum in γ'. Related to the latter, Pt partitions almost solely to the Ni sites in the ordered L12 crystal structure of γ', which has the effect of amplifying the increase in the Al: Ni atom fraction on a given crystallographic plane containing both Al and Ni. Such an effective Al enrichment at the γ' surface kinetically favors the formation of Al_2O_3 relative to NiO. A further contributing factor is that the Pt containing γ'-based alloys show subsurface Pt enrichment during the very early stages of oxidation. This enrichment reduces Ni availability and can increase the Al supply to the evolving scale, thus kinetically favoring Al_2O_3 formation. This observed benefit of Pt addition promoting exclusive Al_2O_3-scale growth is inferred to be a special form of the third-element effect.

The Effect of S and Mn on the High-Temperature Oxidation and Scale Spallation Behavior of Low-Carbon Steels

S. Hayashi, T. Sekimoto, K. Honda, T. Kinoshita, K. Tanaka, K. Ushioda,
T. Narita, S. Ukai

ISIJ International, **49**, 1938-1944, (2009)

Early-stage oxidation behavior in air of low-carbon steels with and without S and Mn additions was investigated in terms of oxidation kinetics and scale spallation in a temperature range of 900 to 1150°C. S and Mn did not appear to affect the growth rate of oxide scales within the given oxidation time, ~30 min, however it was found that S significantly enhanced oxide scale spallation. Scale spallation occurred only on the S doped steels oxidized at temperatures more than 1000°C when the thickness of oxide scale exceeded about 120mm. This scale spallation was confirmed to occur during cooling after the given oxidation time. GD-OES analysis revealed that a significant amount of S enrichment occurred at the oxide/steel interface, which was around 1 mass% on 100ppm S steel after 120s of oxidation at 1150°C. Such sulfur enrichment was speculated to be due to accumulation of rejected S from surface recession during the high-temperature oxidation. Observation of the steel surface after complete removal of the oxide scale by quenching the steels into liquid nitrogen clearly indicates the formation of eutectic Fe–FeS structure at scale/steel interface, resulting from a liquid phase formation above 1000°C. Formation of sulfide, therefore a liquid phase at higher temperature, greatly affected oxide scale spallation.

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

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

Materials Science and Engineering A, **510–511**, 115–120 (2009)

Oxide dispersion strengthened (ODS) ferritic steels, which are the most promising candidate materials for advanced fast reactor fuel elements, have exceptional creep strength at 973K. 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 roomtemperature fromnanoindentation 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.

Y_2O_3 Evolution and Dispersion Refinement in Co-Base ODS Alloys

L. Zhang, S. Ukai, T. Hoshino, S. Hayashi, X. Qu

Acta Materialia, **57**, 3671–3682 (2009)

Co-base ODS alloys are potential materials for high-temperature applications. The evolution of Y_2O_3 during mechanical alloying (MA) and subsequent annealing were studied with the main focus on the refinement of particle size by the addition of minor alloying elements. The results reveal that the MA powder is characterized by ultrafine grains and high dislocation density, which facilitate the decomposition of Y_2O_3. The decomposed Y_2O_3 thermally precipitates at about 690°C. Ti, Zr and Ca cause the coarsening of oxide, while Hf refines the oxide particle size and improves the homogeneity. The optimum Hf content is 1.2 wt.% and the resulting particle size is reduced to 9.6 nm with the precipitation of partially coherent $Y_2Hf_2O_7$ oxides. Higher Al content tends to result in the formation of Al_2O_3 and $Y_3Al_5O_{12}$ oxides, which are of larger size. The threshold stress is predicted to be enhanced by the reduction of inter-particle spacing. The refinement effect is also verified by hardness measurements.

Formation of Ultrafine Grains in 9Cr-ODS Ferritic Steel

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

Heat Treatment and Surface Engineering, **49**, 557-560 (2009)

The high-temperature strength of 9Cr-ODS ferritic steel (Fe-9Cr-0.13C -2W-0.2Ti-0.35Y_2O_3) is owing to the unique structure, residual α-ferrite. In this study, the strength and strength mechanism of the residual α-ferrite are investigated by using nanoindentation technique and transmission electron microscope (TEM). Nano-hardness of the martensite reduces with increasing tempering, whilst the residual α-ferrite maintains higher level of nano-hardness. TEM observation confirmed that the residual α-ferrite contains ultrafine grains. From the selected area diffraction (SAD) study with TEM, the residual ferrite comprises ultrafine grains of 500 nm in size. It is concluded that high nano-hardness and high yield stress in the residual α-ferrite are attributed to the grain refinement strengthening by the ultrafine grains.

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

T. Hoshino, S. Ukai, S. Hayashi

Heat Treatment and Surface Engineering, **49**, 643-646 (2009)

The Ni-10 mass% Y_2O_3 powders were mechanically alloyed for max 100 h by using planetary type of ball-mill. Subsequent heat treatment was conducted at temperature ranging 373 K-1673 K. XRD and hardness measurement were performed in as-MA and heat treated powders. Some of MA powders were hot-pressed at 1473K and 10 kN for 3h, and TEM analysis was performed using their thin foil specimens prepared by electrolytic polishing. In this test, the grain size of Ni matrix is extremely reduced to 50 nm in nano-size, and Y_2O_3 particles are concomitantly dissociated during initial stage of mechanical alloying of 3-10 h. The subsequent heat treatment at temperature beyond 873 K 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 1573 K

Fuel Pin Irradiation Test at up to 5 at% Burnup in BOR-60 for Oxide-Dispersion-Strengthened Ferritic Steel Claddings

T. Kaito, S. Ukai, A. V. Povstyanko, V. N. Efimov

J.Nucl. Scie and Technol., **46**, 529-533 (2009)

The fuel pin irradiation test of the ODS claddings, which were developed as promising materials for higher burnup fuels, was carried out at high cladding temperatures of 700 and 650°C. in BOR-60. Vibro-packed MOX fuels with low O/M ratio were used. The integrity of the ODS cladding fuel pins was maintained up to the burnup of 5.1 at.% and the neutron dose of 21 dpa, and the FCCI of the ODS claddings was very small. These results suggest that the ODS claddings and low O/M ratio fuels are the most appropriate fuel pin systems for high-burnup fuel. The irradiation of ODS cladding fuel pins continues in BOR-60 to a burnup of 15 at.%, and postirradiation data will be acquired.

In-pile Creep Rupture Properties of ODS Ferritic Steel Claddings

T. Kaito, S. Ohtsuka, M. Inoue, T. Asayama, T. Uwaba, S. Mizuta, S. Ukai, T. Furukawa, C. Ito, E. Kagota, R. Kitamura, T. Aoyama, T. Inoue

J. Nucl. Mater., **386-388**, 294-298 (2009)

In order to examine irradiation effect on creep rupture strength of Oxide Dispersion Strengthened (ODS) steel claddings, the in-pile creep rupture test was conducted using Material Testing Rig with Temperature Control (MARICO)-2 in the experimental fast reactor JOYO. Fourteen creep rupture events were successfully detected by the temperature change in each capsule and the gamma-ray spectrometry of the cover gas. Time to creep ruptures of six ODS steel specimens were identified by means of Laser Resonance Ionization Mass Spectrometry (RIMS), and no irradiation effect on creep rupture strength was confirmed within the irradiation condition in the MARICO-2 test.

Effects of Aluminum on High-Temperature Strength of 9Cr-ODS Steel

S. Ohtsuka, T. Kaito, M. Inoue, T. Asayama, S.W. Kim, S. Ukai 1, T. Narita,
H. Sakasegawa

J. Nucl. Mater., **386-388**, 479-482 (2009)

This paper discusses the effects of small amount of Al contamination (<0.1 wt%) on high-temperature strength and microstructure of the 9Cr–ODS steel. Increasing Al concentration degraded the ultimate tensile strength as well as the 0.2% proof stress at 973 K and 1073 K accompanied by decreasing fraction of the elongated grain, i.e., residual-a ferrite acting as reinforcement phase. The decrease of residual-a ferrite proportion provided by increasing Al is contrary to general behavior of conventional steels. Computer simulation on ferrite to austenite phase transformation suggested that the fine oxide dispersion in the elongated ferrite could be attributable to the preferential partitioning of Ti and W in ferrite than in austenite at hot-extrusion process.

Advanced Structural Materials and Cladding

T. Allen, H. Burlet, R. K. Nanstad, M. Samaras and S. Ukai

Materials Research Society, Bulletin, **8**, 20-27 (2009)

Advanced nuclear energy systems, both fission- and fusion-based, aim to operate at higher temperatures and greater radiation exposure levels than experienced in current light water reactors. Additionally, they are envisioned to operate in coolants such as helium and sodium that allow for higher operating temperatures. Because of these unique environments, different requirements and challenges are presented for both structural materials and fuel cladding. For core and cladding applications in intermediate-temperature reactors (400–650°C), the primary candidates are 9–12Cr ferritic–martensitic steels (where the numbers represent the weight percentage of Cr in the material, i.e., 9–12 wt%) and advanced austenitic steels, adapted to maximize hightemperature strength without compromising lower temperature toughness. For very high temperature reactors (>650°C), strength and oxidation resistance are more critical. In such conditions, high-temperature metals as well as ceramics and ceramic composites are candidates. For all advanced systems operating at high pressures, performance of the pressure boundary materials (i.e., those components responsible for containing the high-pressure liquids or gases that cool the reactor) is critical to reactor safety. For some reactors, pressure vessels are anticipated to be significantly larger and thicker than those used in light water reactors. The properties through the entire thickness of these components, including the effects of radiation damage as a function of damage rate, are important. For all of these advanced systems, optimizing the microstructures of candidate materials will allow for improved radiation and high-temperature performance in nuclear applications, and advanced modeling tools provide a basis for developing optimized microstructures.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 1) Introduction and alloy design

A. Kimura, R. Kasada, N. Iwata, H. Kishimoto, C.H. Zhang, J. Isselin, P. Dou, J.H. Lee,N. Muthukumar, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9220 (2009)

Cladding material development is essential for realization of highly efficient high burn-up operation of next generation nuclear systems, where high performance is required for the materials, that is, high strength at elevated temperature, high resistance to corrosion and high resistance to irradiation. Oxide dispersion strengthening (ODS) ferritic steels are considered to be most adequate for the cladding material because of their high strength at elevated temperature. In this work, "Super ODS steel" that has better corrosion resistance than 9Cr-ODS steel, has been developed for application to cladding of a variety of next generation nuclear systems. In the following ten papers, the resent experimental results of "Super ODS steel" R&D, which indicate that many unexpected preferable features were found in the mechanical properties of nano-sized oxide dispersion high-Cr ODS ferritic steel. A series of paper begins with alloy design of "Super ODS steel". Corrosion issue requires Cr concentration more than 14wt.%, but aging embrittlement issue requires less than 16wt.%. An addition of 4wt.%Al is effective to improve corrosion resistance of 16wt.%Cr-ODS steel in SCW and LBE, while it is detrimental to high-temperature strength. Additions of 2wt.%W and 0.1wt.%Ti are necessary to keep high strength at elevated temperatures. An addition of small amount of Zr or Hf results in a significant increase in creep strength at 700 ºC in Al added ODS steels. Tube manufacturing was successfully done for the super ODS steel candidates. "Super ODS steel" is promising for the fuel cladding material of next generation nuclear systems, and the R&D is now ready to proceed to the next stage of empirical verification.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 2) Effect of Minor Alloying Elements

S. Ohnuki, N. Hashimoto, S. Ukai, A. Kimura, M. Inoue, T. KaitoT. Fujisawa,
T. Okuda, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9306 (2009)

Oxide dispersion strengthened (ODS) ferritic steels are one of the candidate materials for fuel cladding of next generation nuclear systems because of its strength at high temperatures and good resistance to irradiations. Presently, the effects of alloying elements, such as Cr and Al, on distribution of oxide particle have been investigated to improve materials properties. However, it has been the matter that mechanical properties were affected seriously by coarsening of oxide particles by addition of Al. On the other hand, it has been observed that the addition of IVa family elements leads to finer and more uniform nano-sized oxide dispersion. The purpose of this study is to investigate the effect of minor element addition on the size distribution of oxide particles by transmission electron microscopy (TEM). The chemical compositions of the mechanical alloyed mixed powders were Fe-16Cr-4Al-mY_2O_3-nZr or mHf. The mechanical alloying was carried out for 48 hours under Ar atmosphere, and then the mixed powder was annealed at 1150 C for 2 hours in vacuum. The powders were Ni-plated and made into a plate specimen. TEM disks were prepared from the plate after mechanically-polishing to 50μm thick and finally electro-polished for TEM observations. TEM observation was performed using a 200 kV microscope. On all the observed specimens, oxide particles of ~ 50nm diameter were observed. It was found that the addition of IVa family elements effectively reduced the size of oxide particles. From the result of size and number density measurements, the optimum composition was considered to be 0.35Y_2O_3-0.3Zr and 0.35Y_2O_3-0.6Hf in mass %. It is notable that the oxide formation energy of Zr and Hf is lowest among the IVa elements investigated in this work. The strong affinity may suppress the diffusion of the elements during fabrication process, and then results in the formation of fine oxide particles in high density.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 3) Development of high performance attrition type ball mill

T. Okuda, M. Fujiwara, T. Nakai, K. Shibata, A. Kimura, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9229 (2009)

The mechanical properties of the oxide dispersion strengthened (ODS) ferritic steels at elevated temperatures depend on oxide particle sizes and their interspacing. The formation process of oxide particles is influenced by oxygen content in pre-mixed metal powder or pre-alloyed metal power, where the oxygen was mixed or contaminated during the mechanical alloying (MA) and the following consolidation process. In the present study, a high-performance attrition ball mill was designed and fabricated to make fine MA powder without oxygen contamination from atmosphere. Furthermore, all the manufacturing processes of screening and filling the powder in a capsule for extrusion are performed in the inert gas atmosphere. The optimum excess oxygen contents of the candidate ODS steels can be defined by utilizing these controlled equipments. The effects of titanium, zirconium, hafnium, and oxygen addition on the formation of yttrium based complex oxide particles were investigated for Fe-16Cr-4Al-2W-0.1Ti -0.35Y_2O_3 ODS ferritic steels with the excellent corrosion resistance.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 5) Mechanical properties and microstructure

R. Kasada, S.G. Lee, J.H. Lee, T. Omura, C.H. Zhang, P. Dou, J. Isselin, A. Kimura, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, T. Okuda, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9072 (2009)

Oxide dispersion strengthened (ODS) ferritic steels are promising material for the next generation fission reactor fuel pin cladding. In the present study, the relationship between mechanical properties, such as tensile strength, fracture toughness and ductile-brittle transition behavior, and microstructure of the Al-added ODS ferritic steels were investigated. The mechanism of improvement of creep strength by Zr or Hf addition is also proposed on the basis of the result of TEM observation. The ODS ferritic steels used in the present study were SOC-1 which is a reference material for the SUPER ODS R&D, and its variations with an addition of minor elements, such as Zr and Hf (SOC-14 and 16). The chemical compositions of SOC-1 is Fe (bal.)-16.1Cr-3.4Al-0.09Ti-0.27Y_2O_3 in wt.%. Pre-mixed powders of the compositions were mechanically-alloyed in high purity Ar gas and canned in vacuum. Finally, hot-extrusion was carried out to be about 25 mm diameter at 1150 °C, followed by a heat treatment for 1 hour at 1150 °C. Tensile tests were carried out at room temperature. Sub-sized 1.5 × 1.5 × 20.0 mm V-notch specimens were used for the Charpy impact tests. The crystallographic anisotropy was also investigated by Schulz's reflection method using the Rigaku TTR-III X-ray diffractometer (XRD). Morphology of the nano-scale oxide particles in the ODS steels were also investigated by using field emission transmission electron microscopy (FE-TEM). As one of the results, newly-developed Al-added ODS ferritic steels with Zr or Hf showed much better creep strength than the ODS ferritic steels without Zr/Hf addition. This successful development was achieved by microstructural modification of nano-oxide particles: The addition of Zr or Hf resulted in the reduction and increases of the size and number density of the oxide particles, respectively. Furthermore, the addition of Zr or Hf enhanced the formation of grain boundary precipitation of carbides and oxides in high density. Both effects play important role in the improvement of the creep strength.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 6) Corrosion Behavior in SCPW

J.H. Lee, A. Kimura, R. Kasada, N. Iwata, H. Kishimoto, C.H. Zhang, J. Isselin, P. Dou, N. Muthukumar, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9223 (2009)

Generally, corrosion is a critical issue for cladding materials, especially, in sever corrosion environment like supercritical pressurized water (SCPW). It is also expected that in reactor water chemistry can be influenced by energy particle irradiation. Therefore, it is essential to develop corrosion resistant cladding material for realization of highly efficient high burn-up operation of next generation nuclear systems. In this work, the effects of alloy elements on the corrosion behavior in SCPW were investigated for a series of ODS steels to design alloy compositions for corrosion resistant super ODS ferritic steels. Corrosion tests were carried out for the ODS steels with different concentrations of Cr and Al in SCPW at 400, 500 and 600 ºC at 25MPa. The corrosion of the ODS steel was enhanced by the decrease in the concentration of Cr and Al. In 19Cr-ODS steels, the addition of 4wt.%Al is not effective to improve corrosion resistance, but it is very effective in 16Cr-ODS steels. It was revealed by EPMA measurements that a very thin alumina film was formed on the specimen surface of the Al added ODS steels, which suppressed the corrosion of Al added ODS steels. The addition of Hf resulted in a significant increase in the corrosion rate. However, the corrosion rate was increased a little by the addition of Zr. The corrosion rate of SUS430, which contained 16wt.%Cr, was much higher than 16Cr-ODS steel. This suggests that nano-sized oxide particles dispersion and very fine grains play important role in suppression of the corrosion. A systematic study of the effect of grain size on corrosion rate indicates that the corrosion rate decreases with decreasing grain size below 1□m, while above it, the corrosion rate is not influenced by grain size. Furthermore, the nano-sized oxide particles are also considered to cause the suppression of corrosion in comparison to SUS430. Steady strain rate tests (SSRT) were carried out at 500 ºC for ODS steels. The effects of strain rate on the stress-strain behavior was investigated for the ODS steels. No effect was observed on the stress-strain behavior and fracture mode: in both the case ductile fracture was observed with showing dimples on the fracture surface.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 7) Corrosion Behavior and Mechanism in LBE

H. Sano1, T. Fujisawa1, A. Kimura, M. Inoue, S. Ukai, S. Ohnuki, T. Okuda,
F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9308 (2009)

Corrosion of structural materials is one of the important problems when lead-bismuth eutectics (LBE) is used as coolant material in next generation nuclear systems. In this study, dissolution experiments of synthetic Fe-Cr-Al alloys and developed super ODS steel candidates into LBE under several partial pressures of oxygen were conducted. Dissolution behavior of major components in such steels into LBE was investigated. Interfacial behavior between LBE and steels was also observed. In addition, partial potential diagrams of the Fe-Cr-Al-O system at several conditions were established as basic data. From the potential diagrams, the partial pressure range of oxygen was estimated for the stable protective oxide layer formation at the interface. At lower oxygen partial pressures than the pressure that is adequate for the formation of the stable oxide layer, a rough oxide layer was formed at the interface in all samples, and the ally elements dissolved into LBE through it. On the other hand, at the oxygen partial pressure to form stable oxide layer, a dense and very thin oxide layer was formed especially on the higher aluminum content steel, preventing the alloy dissolution into LBE. From the results, aluminum and chromium content in steel were very important for preventing the corrosion by LBE.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 9) Damage Structure Evolution under Electron-Irradiation

S. Ohnuki, N. Hashimoto, S. Ukai, A. Kimura, M. Inoue, T. Kaito, T. Fujisawa, T. Okuda, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9307 (2009)

ODS ferritic steels are one of the candidate cladding materials of the advanced fission reactors, because of their good mechanical properties and the irradiation resistance. It is expected that the nano-scaled fine oxide particles are the key of the good performance of the steels. However, no information is available for the effects of nano-scaled oxide particles on the formation of irradiation damage structures. In this study, an in-situ TEM observation of microstructure evolution was carried out to investigate the effects of nano-scaled oxide particles on the formation of dislocation loops. The materials compositions were $16Cr-0.35Y_2O_3$ for standard, and the others were added with minor elements of Ti, Zr and/or Hf. The elemental powders were mechanically alloyed, hot-extruded, and followed by a heat-treatment at 1150 ºC. Electron-irradiation and in-situ observations were performed at 500 ºC to 10 dpa by using high voltage electron microscope of Hokkaido University, operated at 1250 kV. The irradiated area was 2 μm in diameter and the thickness was measured by the number of diffraction fringes. The characterization of the oxide particles was performed by SADP, high resolution image and FFT/IFFT methods. In all of steels, black dots-like fine dislocation loops were formed during the irradiation, and the evolution behavior depended on the type of additional elements but not sensitive to the heat-treatment conditions. Standard steel showed clear formation of the loops that grew to 90 nm at this condition. The steel without Al, the loop formation was not well progressed. In case of the steels added with Zr or Hf, they showed an intensive suppression of the loop growth, as we expected from the results of the model alloy experiment. The results indicate that a large number of oxides enhanced the mutual recombination of the interstitials and vacancies, especially at the particles/matrix interfaces. The particles were identified as complex oxide of Y and added elements which have high affinity to oxygen. It was also confirmed that all of the particles were not changed in the size during the irradiation, indicating high irradiation-resistance at this condition.

Super ODS Steels R&D for Fuel Cladding of Next Generation Nuclear Systems 10) Cladding Tube Manufacturing and Summary

S. Ukai, S. Ohnuki, S. Hayashi, T. Kaito, M. Inoue, A. Kimura, T. Fujisawa,
T. Okuda, F. Abe

Proc. of Int. Conf. on Advanced Power Plant, Paper 9232 (2009)

The high Cr oxide dispersion strengthened (ODS) ferritic steels with superior corrosion resistance have been developing for the fuel elements of the next generation nuclear energy system. In order to realize the prospective super ODS fuel element, cladding tube manufacturing is a crucial technology. In this study, recrystallization behavior of the ODS sheet specimens as well as practical tubes was investigated with repeating a set of cold rolling and heat treatment. Cold–rolling and recrystallization tests were performed using sheets, which were cut from the extruded bar of the standard ODS steel. At 50 % reduction rate, Vickers hardness is around 350 Hv. Only some dislocation recovery occurs after 1 hour heat treatment below 1100 ºC, while above this temperature recrystallization being concomitant with hardness reduction to 250 Hv occurs. The cold rolled texture shows <110> axis parallel to the rolling direction and mainly {111} plane along the rolling section with slightly inclining to {001}. This texture is drastically changed to recrystallized texture, which is <100> axis parallel to rolling direction and {110} plane along the rolling section. From the mother tubes in the dimension of 18 mm outer diameter and 3 mm thickness, cladding tubes with 8.5 mm OD and 0.5 mm TH were manufactured by using pilger–mill. The cold rolling was repeated four times with each reduction rate of 40–50 %, and intermediate heat treatment was performed. The intermediate heat treatment temperature was shifted from 1100 ºC to 800 ºC after 1st , 2nd and 3rd cold–rolling. The final heat treatment was successfully conducted at 1150 ºC for 1h to make perfectly recrystallized structure. Through this test, it was demonstrated that super ODS steels have an adequate capability for cladding manufacturing. The ODS steel, 16Cr-4Al-2W-0.1Ti added with small amount of Zr(Hf), is the prime candidate of “Super ODS steel” which has high strength at elevated temperatures, high resistance to corrosion in SCPW and LBE, and high resistance to irradiation. Tube manufacturing was also successfully done for the Super ODS steel. It is considered that Super ODS steels R&D is facing to the next stage of verification experiment towards realization of fuel pins of next generation nuclear systems.

In-situ TEM Observations of the Crystallization Process of Solution-Prepared MoS_2 Amorphous Particles

Akinori Hanzawa, Toshihiro Shimada, Tatsuya Hasegawa, Takahiro Sato, Takeo Kamino and Tetsu Yonezawa

Journal of Nanoscience and Nanotechnology, **9**, 6736-6740 (2009)**.**

The crystallization of polymer-mixed amorphous molybdenum sulfide was observed in-situ by a TEM equipped with a heated specimen holder. High electron beam irradiation induced the formation of a crystal structure with a lattice spacing of 0.62 nm, which corresponds to the layer spacing of MoS_2. With a lower electron dose, a possible new crystal structure of molybdenum sulfide with several fringe spacings was identified at room temperature. An ordered layered structure Of MoS_2 appeared after annealing at 600 °C. The completely different crystal phase found here might be responsible for the high temperature required for the formation of the MoS_2 layered structure.

Sulfonate Group-modified FePtCu Nanoparticles as a Selective Probe for LDI-MS Analysis of Oligopeptides from a Peptide Mixture and Human Serum Proteins

Hideya Kawasaki, Akira Tarui, Takehiro Watanabe, Kazuyoshi Nozaki, Tetsu Yonezawa, and Ryuichi Arakawa

Analytical and Bioanalytical Chemistry, **395**, 1423-1431 (2009)

Bare FePtCu nanoparticles (NPs) are first prepared for laser desorption/ionization mass spectroscopy (LDI-MS) analysis as affinity probes to selectively trap oppositely charged analytes from a sample solution. Our present results demonstrate bare FePtCu NPs to be a potentially useful matrix for surface-assisted laser desorption/ionization mass spectroscopy (SALDI-MS), for the analysis of small proteins and peptides. The upper detectable mass range of peptides was approximately 5 kDa, and the detection limit for peptides approximately 5 fmol. Sulfonate group-modified FePtCu nanoparticles (FePtCu-SO_3^- NPs), with ionization being independent of the solution pH, can interact with a positively charged analyte, and the analyte-bound NPs can be separated from the reaction supernatant by centrifugation or an external magnetic field. An oligopeptide, Gly-Gly-Tyr-Arg (GGYR) from an oligopeptide mixture containing Asp-Asp-Asp-Asp (DDDD), Gly-Gly-Gly-Gly (GGGG) and GGYR, was detected using SALDI-MS with FePtCu-SO_3^- NPs employing electrostatic interaction. Furthermore, FePtCuSO_3- NPs can detect lysozyme (Lyz) in human serum through the electrostatic attraction between positively charged Lyz and FePtCu-$SO_3^{(-)}$ NPs at pH 8, while detection of negatively charged albumin in human serum is not possible.

In-situ observation of silver nanoparticle ink at high temperature

Tetsu Yonezawa

Bio-Medical Materials and Engineering, **19**, 29-34 (2009)

In-situ TEM (transmission electron microscopy) of silver nanoparticle ink at high temperature was carried out. Into a carbon film tube coating the spiral tungsten filament which was attached to the TEM specimen holder, a silver nanoparticle ink was injected. After evaporation, silver nanoparticles with an aggregated structure could be observed. The temperature of the tungsten wire can be controlled by DC current supplied by dry batteries. Fusion of smaller nanoparticles was observed at a higher temperature and some particles were incorporated to larger particles. This technique can be generally used to consider the sintering temperature of such metal nanoparticles.

Detailed Investigation on the Possibility of Nanoparticles of Various Metal Elements for Surface-Assisted Laser Desorption/Ionization Mass Spectrometry

Tetsu Yonezawa, Hideya Kawasaki, Akira Tarui, Takehiro Watanabe, Ryuichi Arakawa, Toshihiro Shimada, and Fumitaka Mafuné

Analytical Sciences, **25(3)**, 339-346 (2009). **Selected as a Hot Article**

In this paper, we describe systematic detailed considerations of the feasibility of using various metal nanoparticles for organic-matrix-free surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS). In order to avoid the influence of organic molecules on the nanoparticles, stabilizer-free bare nanoparticles of Ag, Au, Cu and Pt were prepared by laser ablation. Although all metal nanoparticles absorbed N_2 laser light (337 nm) energy, the performance of desorption/ionization of a representative peptide, angiotensin I, strongly depended on the metal element. Citrate buffer was used as a proton source; it reduced the amount of alkali cation adducts present. Then, protonated molecules of analytes predominated in the mass spectra when Au and Pt nanoparticles were used. Pt nanoparticles showed the highest performance in SALDI-MS, owing to their smaller heat conductivity and higher melting temperature. The selective desorption of a cationic surfactant with longer alkyl chains and a peptide with methionine was also observed.

Plugging a Molecular Wire into Photosystem I: Reconstitution of the Photoelectric Conversion System on a Gold Electrode

Nao Terasaki, Noritaka Yamamoto, Takashi Hiraga, Yoshinori Yamanoi, Tetsu Yonezawa, Hiroshi Nishihara, Tsutomu Ohmori, Makoto Sakai, Masaaki Fujii, Akihiko Tohri, Masako Iwai, Yasunori Inoue, Satoshi Yoneyama, Makoto Minakata, Isao Enami

Angewante Chemie-International Edition, **48(9)**, 1585-1587 (2009)

Photoinduced electron transfer occurs from photoexcited P700 in photosystem I (PSI) to a gold surface (see picture). A novel molecular connector system is used, in which an artificial molecular wire, which is assembled on the gold surface, was plugged into PSI by reconstitution. Analysis of the photoelectron transfer kinetics proved both the output of electrons from PSI and the effectiveness of the molecular wire.

Gold-Nanoparticle-Supported Silicon Plate with Polymer Micelles for Surface-Assisted Laser Desorption/Ionization Mass Spectrometry of Peptides

Akira Tarui, Hideya Kawasaki, Takuma Taiko, Takehiro Watanabe, Tetsu Yonezawa, and Ryuichi Arakawa

Journal of Nanoscience and Nanotechnology, **9**, 159-164 (2009).

We developed surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS) using nanocomposite films of cationic diblock copolymer micelles [poly(styrene-*b*-N-methyl-4-vinyl pyridinium iodide)] and ammonium citrated Au nanoparticles (AuNPs) on silicon. The nanocomposite film on silicon was suitable for use as a material for matrix-free LDI-MS of peptides due to its low matrix background from Au clusters and high ionization efficiency; this plate successfully ionized angiotensin I, and also insulin in the proton adduct forms, in contrast to methods using only AuNPs and those using nanocomposite films of cationic polymer in conjunction with Au NPs. The high ionization efficiency is discussed from the viewpoint of nanoparticle distribution controlled by polymers on the plate (aggregates vs. nonaggregates).

Basic and Recent Topics of Metal Nanoparticles

Atsushi Hyono and Tetsu Yonezawa

Shikizai Kyokai Shi, **82**, 468-474 (2009)

This is a review article on basic and recent topics of metal nanoparticles (Japanese).

Palladium nanoparticle seeded electroless metallization of Al/Al_2O_3 surfaces

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

Materials Letters, 63, 1451- 1454 (2009)

A simple method for the formation of palladium nanoparticles on aluminum and aluminum oxide surface is demonstrated. In the present method, the palladium nanoparticles obtained directly on the solid surface by immersing the specimen in palladium(II)acetate solution followed by reduction to metallic palladium by using sodium hypophosphite. In the investigation, as-received, boiled, electropolished and anodized aluminum was used as substrate. Additionally, the method is combined with the electroless nickel plating, which facilitates two steps metallization technique on the respective surfaces. In these cases, specimens were first immersed in palladium(II)acetate solution followed by immersion in electroless nickel plating solution, where, palladium reduced on the specimen surface providing catalytic site for the subsequent electroless nickel deposition. Using the technique, about 6 to 8.5 μm thick Ni–P metallic layer was deposited on the specimen surface.

Growth of multioxide planar film with the nanoscale inner structure via anodizing Al/Ta layers on Si

A. Mozalev, A.J. Smith, S. Borodin, A. Plihauka, A.W. Hassel, M. Sakairi, H. Takahashi1,

Electrochimica Act, 54, 935-945 (2009)

An Al/Ta bilayer specimen prepared by a successive sputter-deposition of a 150-nm tantalum layer and a 180-nm aluminium layer onto a silicon wafer is anodically processed in a sequence of steps in oxalic acid electrolytes, at voltages of up to 53 V, which generates a 260-nm alumina film with well-ordered nanoporous structure. Further potentiodynamic reanodizing the specimen to 220 V causes the simultaneous growth of a 65-nm tantalum oxide layer beneath the alumina film and an array of oxide ‘nanocolumns’ (50 mn wide, 80 nm apart, 7×10^9 cm^{-2} population density) penetrating the alumina pores and reaching precisely to the top of the alumina film. The complete filling of the alumina pores is assisted by the high Pilling–Bedworth ratio for Ta/Ta_2O_5 and a substantially increased transport number for tantalum species (0.4), which is an average value of all migrating tantalum ions with different oxidation states. The nanocolumns are shown to be composed of a unique, regular mixture of Ta_2O_5 (dominating amount), suboxides TaO_2 and TaO_x ($0.5 < x < 1$), Al_2O_3, metallic Ta and Al aggregates, tantalum diboride (TaB_2) and oxidized boron from the electrolyte. The ionic transport processes determining the self-organized growth of these planar oxide nanostructures are considered and described conceptually.

Growth of porous type anodic oxide films at micro-areas on aluminum exposed by laser irradiation

Tatsuya Kikuchia, Masatoshi Sakairia and Hideaki Takahashi

Electrochimica Acta, 54, 7018-7024 (2009)

Aluminum covered with pore-sealed anodic oxide films was irradiated with a pulsed Nd–YAG laser to remove the oxide film at micro-areas. The specimen was re-anodized for long periods to examine the growth of porous anodic oxide films at the area where substrate had been exposed by measuring current variations and morphological changes in the oxide during the re-anodizing. The chemical dissolution resistance of the pore-sealed anodic oxide films in an oxalic acid solution was also examined by measuring time-variations in rest potentials during immersion.

The resistance to chemical dissolution of the oxide film became higher with increasing pore-sealing time and showed higher values at lower solution temperatures. During potentiostatic re-anodizing at five 35-μm wide and 4-mm long lines for 72 h after the film was removed the measured current was found to increase linearly with time. Semicircular columnar-shaped porous type anodic oxide was found to form during the re-anodizing at the laser-irradiated area, and was found to grow radially, thus resulting in an increase in the diameter. After long re-anodizing, the central and top parts of the oxide protruded along the longitudinal direction of the laser-irradiated area. The volume expansion during re-anodizing resulted in the formation of cracks, parallel to the lines, in the oxide film formed during the first anodizing.

Effect of Potential, Temperature, and Fluoride Ions on the Repassivation Kinetics of Titanium in Phosphate Buffered Saline Solution with the Photon Rupture Method

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

Laser chemistry, 2009, Article ID 436065, 8 pages, (2009)

The effect of the applied potentials, temperature, and F^- ions on the localized repassivation kinetics of titanium was investigated by the photon rupture method, PRM, and electrochemical techniques in phosphate buffered saline solution. The log I vs. log t plots after laser beam irradiation showed a rapid increase, then a decrease with a slope of about -1.5, which is steeper than that expected from high field oxide film formation theory, suggesting that the repassivation of titanium is a combination of electrochemical and chemical reactions. The repassivation current increases with increases in the applied potential and addition of F- ions, while solution temperature does not influence the repassivation kinetics. The effect of F- ions on the repassivation kinetics can be explained by localized pH changes caused by very rapid dissolution of titanium when titanium was exposed to PBS solution.

Metallization of Oxide / Hydroxide Film of Aluminum: the Palladium Activation Techniques,

Himendra Jha, Tatsuya Kikuchi, Masatoshi Sakairi, and Hideaki Takahashi,

J. Surf. Finsh. Soc. Jpn., 60, 208-212 (2009)

Palladium-activation-based techniques for area-selective microscale metallization on porous oxide film of aluminum and complete metallization of the oxide/ hydroxide surface of aluminum are demonstrated. For area-selective metallization, a porous anodic oxide film of aluminum was colored in an organic dye solution containing small amounts of palladium acetate. It was then hydrothermally sealed, thereby trapping the palladium acetate underneath the newly formed crystalline hydroxide layer. Removal of the surface hydroxide layer using a laser beam, exposes the palladium acetate, which also undergoes photothermal decomposition and reduction to metallic palladium and acts as a catalytic center for subsequent electroless plating. Similarly, complete metallization of the porous oxide and hydroxide of aluminum were performed by adsorbing palladium acetate onto the surface, followed by electroless nickel plating of the specimen. Here, palladium acetate (on the surface) was first reduced to metallic palladium by the hypophosphite that is present in electroless plating solution, providing a catalytic center subsequent electroless nickel deposition.

Formation of Three-dimensinal Micro-actuators with Polypyrrole/Gold Bi-layer Structure

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

J. Surf. Finsh. Soc. Jpn., 60, 335-341 (2009)

Three-dimensional micro-actuators consisting of a polypyrrole (PPy)/Au bi-layer, were fabricated by Al anodizing, laser irradiation, and electrochemical techniques. Aluminum specimens covered with porous type oxide films were irradiated with a pulsed Nd-YAG laser to remove the oxide films locally. Then an Au layer and a PPy layer were deposited at the area where the film had been removed. Finally, the specimens were immersed in a NaOH solution after connection with or without a Pt plate to separate PPy/Au actuators from the Al substrate and anodic oxide film. The PPy layer did not lose its electroconductivity when the specimen was immersed in NaOH solution after connection with a Pt plate, although the conductivity was lost after immersion of the specimen alone. Immersion with the Pt connection suppressed the PPy reduction and enabled the fabrication of PPy/Au actuators. Three-dimensional PPy/Au bi-layer micro-actuators were fabricated using column Al specimens. They are much more flexible than PPy/Au/resin three-layer actuators described in a previous paper. [Japanese]

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

ECS Trans., **16**, 19-21 (2009)

A Photon Rupture Method (PRM focused pulsed Nd-YAG-laser irradiation to remove materials) was applied to investigate effect of aspect ratio of a pit on its growth rate and direction. It is possible to form artificial micro-pit on aluminum by PRM, and the aspect ratio changes from 0.45 to 1.25 with irradiation time. The current of formed micro-pit at constant potential increases with irradiation time at constant potential. This result is good agreement with previous pitting corrosion research results.

Electrochemical Noise Analysis of 13 mass% Cr Stainless Steel HAZ by Solution Flow Type Micro-droplet Cell
- Effect of solution concentratin-

M. Sakairi, T. Nakayama, T. Kikuchi, S. Hashizume and K. Fushimi,

ECS Trans. **16**, 281-290 (2009)

Low Carbon- 13 mass% Cr martensitic stainless steels have been widely used for line pipe application because of their high strength and excellent corrosion resistance in corrosive conditions. Newly developed solution flow type micro-droplet cell was applied to investigate electrochemical behavior of heat affected zone (HAZ) of 13 mass% Cr stainless steel. This technique makes it possible to measure electrochemical behavior of very narrow area of HAZ. Effect of solution pH and stress on corrosion potentials, and current at constant potential for HAZ portion of welded joints were focused. The corrosion potential at HAZ and base metal shows almost same tendency, however, current change shows clear corrosion resistance difference at HAZ and base metal.

The Effect of Surface Condition and Solution Composition on the Repassivation Behavior of Titanium Studied by PRM in Vitro

M. Sakairi, H. Miyata, M. Kinjyo and T. Kikuchi

ECS Trans., 25, 37-45 (2009)

The effect of surface condition and solution composition on the localized repassivation kinetics of titanium was investigated by the photon rupture method, PRM, and electrochemical techniques in aqueous electrolyte. The log I vs. log t plots after laser beam irradiation showed a rapid increase, then a decrease with a slope of about -1.5, which is steeper than that expected from high field oxide film formation theory, suggesting that the repassivation of titanium is a combination of electrochemical and chemical reactions. The repassivation current increases with increases in the applied potential and suppressed with hydroxylapatite (HAp) coating, while solution compositions does not influence the repassivation kinetics. The effect of HAp coating on the repassivation kinetics can be explained by localized pH changes caused by dissolution of HAp.

Galvanic Corrosion Behavior of 3003 Aluminum Alloy in Model Tap Water

M.Sakairi, A. Kaneko,T. Kikuchi, Y. Seki, and D. Nagasawa

Proc. of Eurocorr2009, paper No. SS 17-O-7947 (2009)

Galvanic corrosion behavior of 3002 aluminum ally in model tap waters was examined by electrochemical noise technique. In all model tap waters, after specimen was connected to Pt cathode 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+}.

Effect of PWHT on Electrochemical Behavior of Low C - 13%Cr Welded Joints with the Use of a Solution Flow Type Micro-Droplet Cell

S. Hashizume, T. Nakayama, M. Sakairi and K. Fushimi
NACE 2009 Paper No.09089 ('2009)

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 have been published. Electrochemical analysis of weld joints is expected to be effective in understanding the crack mechanism. In this paper, electrochemical behavior of low C – 13%Cr weld joints with and without PWHT was evaluated with the use of a solution flow type micro-droplet cell. In this unique technique, a droplet of around 0.2mm diameter is used as an electrochemical cell and it enables local electrochemical measurements. PWHT leads to more noble and stable potential in HAZ compared to as-welded condition. In the HAZ portion of the as-welded joint, Cr depleted zone was detected under welding scale with the use of GDS (Glow Discharge Spectrometer). This can be an initiation of SCC near girth welded joint in hot acid environment. The reason why a polished specimen did not show any SCC is also given.

Highly Uniform Aluminum Oxy-hydroxide Nanofiber from Porous Anodic Alumina

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

ECS Trans., **16**, 2009 (2009)

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.

Effect of the Electrodeposition Temperature on the Cyclic-Oxidation Resistance of Ni Aluminide Containing Zr Formed by Molten-Salt Electrodeposition

M. Fukumoto, T. Suzuki, M. Hara and T. Narita

Materials Transactions, **50**, 335-340 (2009)

The effect of the Al electrodeposition temperature on the cyclic oxidation resistance of Ni aluminide containing Zr formed by molten salt electrodeposition was investigated. Zr and Al were deposited by molten salt electrolysis. For the sample treated with the Al deposition at 1073 K, a layer consisting of Ni_2Al_3 was uniformly formed. On the other hand, for the sample treated by Zr deposition, followed by Al deposition at 1073 K, a layer consisting of Ni_2Al_3 and a Ni aluminide layer containing Zr on the Ni_2Al_3 layer were formed. Furthermore, when the Al electrodeposition temperature was changed, the concentration of Zr in the Ni aluminide layer containing Zr changed. When the Al electrodeposition was carried out at 1153 and 1173 K, the Zr was scarcely observed in the surface region of the Ni aluminide layer. The cyclic oxidation test showed that for the sample treated with only the Al deposition and the sample treated with the Zr deposition, followed by Al deposition at 1073 K, a mass reduction due to scale exfoliation took place, whereas for the samples treated with the Zr deposition, followed by Al deposition at 1153 and 1173 K, no mass reduction was observed. For these samples, after the cyclic oxidation test, a scale consisting of α-Al_2O_3 adhering to the substrate was formed. Consequently, it was found that the cyclic oxidation resistance of Ni was improved by Zr deposition, followed by Al deposition at 1153 and 1173 K.

Experimental and Simulation Study of Uphill Diffusion of Al in a Pt-Coated γ-Ni-Al Model Alloy

B. Sundman, S. Ford, X-G. Lu, T. Narita, and D. Monceau

J. Phase Equilibria and Diffusion, **30**, 602-607 (2009)

An experimental study of diffusion of Al, Ni, and Pt in a Pt-coated binary Ni-Al alloy has been made and compared with a computer simulation. Assessed thermodynamic and kinetic descriptions have been used. Starting from the measured experimental concentration profiles after 1 h heat treatment at 1173 K the simulation is compared to the experimentally determined profiles after 11 h continuous heat treatment. The experimental finding that Al will diffuse against its concentration gradient is explained by the strong lowering of the chemical potential by Pt. The simulation predicts that Al will reach a concentration maximum at the surface, larger than its bulk composition.

Density Functional Theory Study of Zinc Clusters

Kei Iokibe, Takeshi Sakamoto, Hiroto Tachikawa and Kazuhisa Azumi

J. Surface Finishing Soc. Japan, **60**, 592-597 (2009)

Ab initio molecular orbital (MO) and density functional theory (DFT) calculations were applied to zinc clusters comprising 2-192 atoms. The minimum bonding length, average binding energy, and electron population of the 4p orbital (N_{4p}) were evaluated as a function of the number of atoms (n) after optimization of the cluster structure. The clusters show a drastic transition in their properties from molecular to clusters at around n=4, and gradually exhibit bulk properties with increasing n. Polarization of the clusters' electric charge was also predicted—negative charging inside the cluster and positive charging at the surface—attributable to nonuniform distribution of electrons belonging to the orbits of respective atoms. The highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO-LUMO) transition energy gap with changing n, the relation between the N_{4p} value, the cluster stabilization energy, and the influence of defects in the crystalline N_{4p} are also discussed. (Japanese)

DFT Calculation of Surface Diffusion of Zinc Adatom on Zinc Crystal Surface

Kei Iokibe, Takeshi Sakamoto, Hiroto Tachikawa and Kazuhisa Azumi

J. Surface Finishing Soc. Japan, **60**, 453-458 (2009)

Ab initio molecular orbital (MO) and density functional theory (DFT) calculations were applied to surface diffusion analysis of a zinc adatom on a zinc (001) surface. An energetic contour map for surface diffusion of adatoms on surfaces of terrace, step, and kink sites were drawn to evaluate the activation energies for surface diffusion of each path. These sites' potential energies were higher in the order of terrace, step, and kink. The activation energy for surface diffusion on the terrace and through the step is considerably low. These results were consistent with the general terrace–step–kink model proposed for epitaxial growth during metal deposition. Validation of activation energy obtained by MO calculation is discussed along with remaining problems of MO calculation applied to electrochemical systems. (Japanese)

Development of a pH-Sensitive Film Using a Porous Anodic Oxide Film on Al

F. Nishiyama, H. Konno, K. Azumi

J. Surface Finishing Soc. Japan, **60**, 186-189 (2009)

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 a pH-indicator reagent and boiled to seal it in the film. Litmus, bromthymol blue (BTB), and Congo red were used as pH-indicator reagents. The film, containing litmus, changed 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. For example, the film containing BTB prepared with long sealing time appeared to be green in an alkaline solution because of mixing of blue at the surface and yellow inside the film. Optimization of film thickness, the choice of pH-indicator reagent, and sealing conditions are important to prepare a highly pH-sensitive film

Electroless Ni-P Deposition on AZ91 D Magnesium Alloy Prepared by Molybdate Chemical Conversion Coatings

H. H. Elsentriecy, K. Azumi

J. Electrochem. Soc., **156**, D70-D77 (2009)

In this study, electroless nickel-phosphorus plating with good adhesion strength was deposited on AZ91 D magnesium alloy prepared with environmentally acceptable molybdate chemical conversion coatings (Mo coatings). Energy dispersive X-ray spectroscopy (EDX) of Mo coatings revealed that the conversion films were mainly composed of $Mg_2Mo_3O_{11}$ particles. The Mo coating showed a rough surface reflected by the non-uniform dissolution of a and b phases of the AZ91 D Mg alloy during the conversion process. Such a rough surface provided excellent adhesion strength of the plating layer to the Mo undercoating layer, reaching more than 18 MPa as measured by the pull-off method due to the anchor effect. Scanning electron microscopy (SEM) results showed that the plating layer over Mo coatings was also rough but compact and almost pore-free. Corrosion tests using potentiodynamic polarization in 3.5 wt.% NaCl aqueous solution indicated that the electroless Ni–P-plated AZ91 D Mg alloy showed a significant improvement in corrosion resistance compared with the corrosion resistance of uncoated specimens.

Direct Reduction of Liquid V_2O_5 in Molten $CaCl_2$

Y. Oka, and R.O. Suzuki

ECS Transaction, **16**, 255-264 (2008)

An alternative process of the reduction of V_2O_5 was studied using molten salt. It consists of thermochemical and electrochemical reactions in molten $CaCl_2$ + CaO. V_2O_5 is thermochemically reduced by Ca. The by-product CaO is electrolyzed to the reductant Ca in the molten $CaCl_2$. Liquid V_2O_5 was reduced to vanadium metal through intermediate CaV_2O_4, and oxygen concentration was 1860ppm at minimum. By deoxidation of the sample with a smaller specific surface area, the lowest oxygen concentration, 460 ppm, could be achieved. A major component of ejected gas from the anode was CO_2 at the initial stage and CO at the later stage. O_2 gas was not detected because its concentration was lower than detection limit.

Calciothermic Reduction of $TiCl_4$ Gas during the Electrolysis of $CaCl_2$ Melt

R.O. Suzuki and T. Naito

ECS Transaction, **16**, 265-270 (2008)

The calciothermic reduction of $TiCl_4$ gas was studied firstly by using Ca-$CaCl_2$ melt, to whose surface the gas was blown. The fine Ti particles settled down in the crucible, when the concentration of dissolved Ca was greater than 2 mol% at 1173 K. When the concentration was less than 2mol%Ca, a part of $TiCl_4$ gas was dissolved probably as $TiCl_3$ or $TiCl_2$ into the $CaCl_2$ melt, and it precipitated as the lower Ti oxides. When $TiCl_4$ gas was blown to the molten $CaCl_2$, which was electrochemically decomposed into Cl_2 gas at the carbon anode and Ca at the Ti cathode, $TiCl_4$ gas was reduced to the dendritic Ti on the cathode surface. Because the electrolyzed Ca reacted preferentially with the oxide crucibles, most of the oxygen ions combined with Ti(II) and Ti(III), and they formed TiO and Ti_2O_3.

Production Methods of Titanium at Present and in Future

R.O. Suzuki

“Fundamentals and Current Applications of Titanium” Ed. by M. Niinomi, CMC Press, Tokyo, 26-39 (2009).

The production methods for metallic titanium are reviewed. Only Kroll method is taken as the industrial standard from various possible methods. Kroll method bases on the chlorination of titanium oxide in the fluidized bed, distillation of $TiCl_4$, magnesium reduction of $TiCl_4$, and electrolysis of $MgCl_2$. Although the modernized Kroll method can produced 10 ton per batch for several days, it is still not comparable to the mass production of iron making. To establish a strong industrial position of Ti production in the world, the Japanese companies try to improve the processing and raw materials. These efforts are briefly reviewed.

Many ideas on new production method and their experimental efforts are tentatively collected and introduced from the thermodynamical aspects. On the requirements from industrial situation and natural resouces, titanium oxides are commonly taken as the starting materials. The assistance by the electrical energy is indispensable, and the high temperature operation is needed to enhance the production rate. The molten salt technology or the gaseous chemical reactions can solve these severe demands. FFC process and OS process are characteristic ideas to face the molten salt electrolysis. Some reasonable solutions are now approaching to the pilot plant level, but simultaneously they meet many serious problems for industrialization. The wisdom and knowledge accumulated in this field are reviewed. (Japanese)

Calciothermic Reduction and Simultaneous Electrolysis of CaO in the Molten $CaCl_2$

R.O. Suzuki

Proc. Processing Materials for Properties III Ed. by B. Mishra, A. Fuwa, and P. Bhandhubanyong, ISBN:978-0-87339-727-8, TMS (The Minerals, Metals & Materials Society, USA), 387-392 (2008)

The combination of the calciothermic reduction and simultaneous electrolysis of CaO in the molten $CaCl_2$ (so-called OS process) was applied to the metal production of Ti and V. The pure Ti and V containing about 4000 mass ppm oxygen was successfully obtained by controlling the supplied charge to form Ca efficiently. The Ti-Al-V alloy powder was also produced from the mechanically mixed oxides, and the distribution of metallic components could be homogenized by sintering after removal of the solidified $CaCl_2$.

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

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

Materials Transactions, **50**, 2704-2708 (2009)

Titanium dioxide (TiO_2) was successfully reduced at 1223 K by calcium, which was deposited due to the molten salt electrolysis of CaO dissolved in the molten $CaCl_2$. The current density and the Ca concentration near the cathode were varied by changing the electrodes' surface areas and the distances between an anode and cathode, respectively. At the initial stage of reduction, metallic Ti powder with a lower oxygen concentration was obtained at a lower current density; in this case, most of the electrochemically deposited Ca was efficiently used for reduction. Meanwhile, at the final stage of deoxidation, Ti powder with a much lower oxygen concentration was obtained at a higher current density. In order to obtain metallic powder with a low oxygen concentration, the formed Ca should penetrate the inner part of the sintered sample.

Direct Metal Production from Oxides by Using Molten Salt Electrolysis of CaO in $CaCl_2$

R.O. Suzuki

Proc. Processing and Fabrication of Advanced Materials XVIII, Ed. by M.Niinomii, M.Morinaga, M.Nakai, N.Bhatnagar and T.S.Srivatsan, **2**, 701-710 (2009)

Molten salt electrolysis of CaO dissolved in the $CaCl_2$ melt can generate the reactive Ca atmosphere near the cathode, which has a strong reducing ability equivalent with pure Ca. When the oxide is set inside the basket-type cathode, it is reduced to the corresponding metal. The applied voltage should be controlled between 1.6 and 3.2 V above the melting temperature of $CaCl_2$ (1053K), when a carbon anode is used. The formed by-product CaO is removed as CO and CO_2 gas at the carbon anode. Within 3 hours we can obtain pure α-Ti from the starting TiO_2 powder in $CaCl_2$-0.5mol%CaO melt. As increasing the supplied charge, the residual oxygen in Ti decreased.

This simple mechanism has been successfully applied for production of 12 kinds of metals such as Ti, Zr, V, Nb, Cr, Fe, etc. However, the rare earth metals such as Y and Er could not be obtained due to thermodynamic limitation of calciothermic reduction. MgO, In_2O_3 and SnO_2 formed their metallic liquid.

Direct Production of Ti-29Nb-13Ta-4.6Zr Biomedical Alloy from Oxide Mixture in Molten $CaCl_2$

S. Osaki, H. Sakai and R.O. Suzuki

Proc. Processing and Fabrication of Advanced Materials XVIII, Ed. by M.Niinomii, M.Morinaga, M.Nakai, N.Bhatnagar and T.S.Srivatsan, **2**, 815-824 (2009)

Ti-29Nb-13Ta-4.6Zr(TNTZ) alloy was successfully produced by co-reduction of oxide mixture, which consisted of TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2. This method uses high reducibility of Ca or Ca-condensed molten salt. Ca was produced by controlled-potential electrolysis of CaO in molten $CaCl_2$ under 3.2V at 1173K with carbon anode and Ti cathode. The supplied charge Q was varied in the range of 50~400% of theoretical charge (Q_0) to generate the required amount of Ca to reduce the oxide mixture.

The oxygen concentration of the obtained powder sample decreased monotonously as the supplied charge increased. 1.37 mass% oxygen could be attained at Q/Q_0 =165% and 1900 mass ppm at Q/Q_0 =323%. X-ray diffraction measurements identified the sample which has low oxygen concentration as the mixture of Ti-based BCC solid solution and a small amount of HCP solid solution. The electron probe microanalysis showed that the composition of this sample was slightly different from the targeted composition due to difference of reduction rate of the component oxides. After sintering at 1300K for 54ks, the HCP phase disappeared and the compositional homogeneity was improved within ±3.5mass% to the targeted composition.

Lithium Ion Insertion/Extraction Performance of Si/C/O Composites Formed from Polyimides Containing Silicone

S. Saito, T. Kasashima, K. Fushimi, H. Konno

TANSO, **240**, 207-212 (2009)

Si/C/O composites were formed by carbonization of Kapton type polyimide films containing 0–10 at% Si. About 24 mass% of Si was present in the composite derived from the polyimide containing 7 at% Si at 1350 ºC and, by ^{29}Si MAS NMR, they were mainly $Si(O)_4$ type components around –110 ppm with unidentifiable components in a range of –100 to –20 ppm. This composite showed the best performance of Li^+ ion insertion/extraction: the coulomb efficiency was nearly 100 % except for the 1st cycle and the extraction capacities were 648 mA h g^{-1} after 10 cycles at 50 mA g^{-1} and 393 mA h g^{-1} after 100 cycles at 50 mA g^{-1}, and the latter was increased to ca. 470 mA h g^{-1} by preliminary cycles at low current densities. After 10 cycles at 50 mA g^{-1} the components around –110 ppm almost disappeared from NMR spectrum and a broad and noisy band was observed in a range of –100 to –50 ppm. Since sub-micrometer fused silica particles did not react as the composites performed, the components around –110 ppm are not necessary silica. The mechanism of reversible insertion/extraction of Li^+ ion for the composites was not completely clarified, but the results by cyclic voltammetry and MAS NMR left room for doubt an alloying/dealloying mechanism between Si and Li. (Japanese)

Preparation of Boron-containing Carbons from Glucose-borate Complexes and Their Capacitive Performance

T. Ito, M. Ushiro, K. Fushimi, K. Azumi, H. Konno

TANSO, **239**, 156-161 (2009)

Hydrothemally synthesized glucose-borate complexes (mole ratio 1/1 and 1/2) were carbonized at 800–1200 ºC for 1 h in argon, followed by boiling in water to remove borate byproducts. Formed boron-containing carbons (B-carbons) contained 1–3.4 mass% boron and, by XPS, boron was present mainly as a form of C-B-O bonding and not as the substituted boron. The specific surface area by N_2 adsorption, S_{BET}, was 850–1360 m^2 g^{-1}, and decreased with raising heat treatment temperature. The 1/2 complex provided larger SBET than the 1/1 complex. Pore width was less than 3 nm except for the products at 1200 ºC. The cyclicvoltammograms (CVs) at 2 mV s^{-1} in 1 mol dm^{-3} Na_2SO_4 were rectangular and the specificcapacitance normalized by S_{BET}, C_A, was 0.05–0.1 F m^{-2}, indicating the electric double layer capacitance. In 1 mol dm^{-3} H_2SO_4, CVs showed broad redox peaks in a potential range of 0–0.6 V vs. SCE and C_A was 0.13–0.2 F m^{-2}: the pseudocapacitance is attributed to more than two types of oxygen-containing functional groups and one of them might be =B-OH type. The electrode capacitance, C_M in F g^{-1}, in H_2SO_4 solution was more than twice of the C_M in the Na_2SO_4 solution. It may be mainly due to the difference between Na^+ and H^+ ions, though a certain level of pseudocapacitance is contributing to C_M. Carbons derived from a mixture of poly(vinyl alcohol) and boric acid were $S_{BET} < 50$ m^2 g^{-1}, suggesting that the large S_{BET} of B-carbon is owing to the thermal decomposition behavior of glucose-borate complexes, which is different from the pore formation mechanism of the MgO template method reported. (Japanese)

Anodic Dissolution of Titanium in Chloride-containing Ethylene Glycol Solution

K. Fushimi, H. Kondo, H. Konno

Electrochim. Acta, **55**, 258-264 (2009)

Anodic dissolution behavior of titanium in chloride-containing ethylene glycol was examined using a rotating disk electrode. A potential-independent dissolution current flowed depending on the rotation speed, species and concentration of chloride salts. In solutions with lower concentrations of chloride, a potential-independent current was controlled not only by the mass transfer process but also by the charge transfer, and the kinetic-controlling current depends on solution conductivity. In concentrated chloride solutions, the current was controlled only by mass transfer process and decreased with increase in chloride concentration. A smaller current also flowed in a solution with a high concentration of titanium species. These results indicated that the diffusion-controlling species are titanium species, not chloride ions. Electrochemical impedance spectroscopy revealed that a titanium chloride salt layer, which maintains titanium species at a high concentration, accumulates a low charge (~0.1 μF cm^{-2}) and becomes thicker with increase in applied potential, is formed between the titanium substrate and diffusion layer during the mass transfer-controlling dissolution.

Capacitance Behavior of Carbonaceous Materials Derived from KAPTON Films Containing Small Amounts of Metallic Compounds

M. Ushiro, A. Yoneda, N. Iwasa, K. Fushimi, H. Konno

TANSO, **238**, 121-125 (2009)

KAPTON films with and without adding small amounts of metallic compounds (0.1~2 at% as metal) were carbonized at 800 ~ 1200 ºC for 1 h in nitrogen and capacitance was measured in sulfate solutions by cyclic voltammetry. Nitrogen containing carbons derived from the film without additives had low specific surface area ($S_{\mathrm{BET}} < 90$ m^2 g^{-1}) and the capacitance (C_{T}) was lower than 35 F g^{-1}. The capacitance normalized by S_{BET} (C_{SP}), however, reached as high as 0.77 F m^{-2}, and decreased with decreasing nitrogen content (W_{N}), indicating pseudocapacitance due to nitrogen. The correlation between C_{SP} and a proportion of particular nitrogen species on surface was not observed. Except for silicone, the addition of compounds of Fe(II), Co(II),Ni(II), and Ti(IV) increased SBET : S_{BET} increased with increasing amount of additives. The C_{SP} value for the products at 850 ºC varied depending on the additives, and the products were grouped under a) nitrogen-containing carbons mainly showing pseudocapacitance due to nitrogen, b) iron-containing carbons showing redox peaks, and c) carbons having relatively high S_{BET} (around 400 m^2 g^{-1}) and mainly showing the electric double layer capacitance. (Japanese)

Depassivation-repassivation of Type-312L Stainless Steel in NaCl Solution Investigated by the Micro-indentation

T. Yamamoto, K. Fushimi, M. Seo, S. Tsuri, T. Adachi, H. Habazaki

Corros. Sci., **51**, 1545-1553 (2009)

Repassivation behavior of type-312L stainless steel containing 6% of molybdenum was examined in NaCl solution using in situ micro-indentation technique, together with type-304 and 316L stainless steels. High stability of the passive film formed on the type-312L stainless steel was also examined by depth profiling analysis of passive films using glow discharge optical emission spectroscopy (GDOES). In 0.9 mol dm^{-3} NaCl solution at 296 K the type-304 and 316L stainless steels are passive only up to 0.3 V (SHE), above which pitting corrosion occurs. In contrast, no pitting corrosion occurs on type-312L stainless steel. Despite the significant difference of the pitting corrosion resistance, the repassivation kinetics of the three stainless steels, examined by micro-indentation at 0.3 V (SHE), is similar. The presence of molybdenum in the stainless steel does not influence the repassivation kinetics. The charge required to repassivate the ruptured type-312L stainless steel surface increases approximately linearly with the potential, even though the passivity-maintaining current increased markedly at potentials close to the transpassive region. Repassivation occurs without accompanying significant dissolution of steel, regardless of the stability of passive state. Depth profiling analyses of the passive films on the type-312L stainless steels formed at several potentials revealed that molybdenum species enrich in the outer layer of the passive film, below which chromium-enriched layer is present. The permeation of chloride ions may be impeded by the outer layer containing molybdate, enhancing the resistance against the localized corrosion of the type-312L stainless steel.

Limiting Current in a Flowing Electrolyte-type Droplet Cell

K. Fushimi, S. Yamamoto, H. Konno, H. Habazaki

ChemPhysChem, **10**, 420-426 (2009)

Convective mass transfer in a flowing-electrolyte-type droplet cell (f-DC) is investigated for quantitative analysis of an electrode process and precise electrofabrication of microstructures using this device. The limiting current in the f-DC was expressed theoretically and its practical equation is investigated experimentally by cyclic voltammetry in solutions containing a redox mediator. The limiting-current equation in the f-DC derived experimentally could be expressed as a sum of hydrodynamic and stagnant terms. The current derived from the latter term of the f-DC is ten times larger than that in a conventional stagnant cell, thus indicating that the convective mass transfer in the cell would be changed dramatically at a small volumetric flow rate.

The Effect of Metal Texture on Depassivation-repassivation Behavior of Iron in Borate Buffer Solution Investigated by Micro-indentation

T. Yamamoto, K. Fushimi, H. Habazaki, H. Konno, S. Miura

ECS transactions, **16**, 133-140 (2009)

The effects of grain orientation and cold-rolling on the depassivation -repassivation behavior of polycrystalline irons were examined in pH8.4 borate buffer solution using *in-situ* micro-indentation technique. The depassivation rate on the passive iron surface during the downward drive of the indenter (penetration of an indenter tip into iron surface) depended on the grain orientation; the highest rate was obtained on {100} surface, on which a possible main slip plane of {110} was normal to the surface. In contrast, the total electric charge required for repassivation during the downward and subsequent upward drives was not influenced by the grain orientation. The electric charge for repassivation was strongly influenced by the rolling reduction that changed the dislocation density at the specimen surface. There was a linear correlation between the electric charge normalized by residual dent area and the square root of the dislocation density.

Depassivation pH of Austenitic Stainless Steels in NaCl Aqueous Solution

K. Fushimi, K. Takakura, H. Habazaki, H. Konno, K. Azumi, T. Tsuri

ECS transactions, **16**, 291-296 (2009)

The combination of the potentiometric pH measurement and potentiostatic polarization was carried out for the type-312L and 316L austenitic stainless steels during decreasing pH by dropping hydrochloric acid in sodium chloride solution. The acidification changed the surface condition of the austenitic stainless steels. The significant acidity of the solution induced a rapid increase in the anodic current passing through the steel at a critical pH, pH_{depass}. The value of pH_{depass} was increased by elevating the solution temperature or concentrating the chloride ions in solution. In the potential–pH_{depass} diagram, the surface condition could be classified into four domains; immunity, active, passive and transpassive/pitting states. The boundary between the active and passive states was strongly dependent on solution pH but independent of potential, indicating that the depassivation of the steel surface proceeded with a chemical reaction participating protons rather than the electrochemical one.