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

Prof. M. Ueda: LABORATORY OF CORROSION ENGINEERING

Prof. H. Habazaki: INTERFACIAL ELECTROCHEMISTRY LABORATORY

Prof. K. Kurokawa: LABORATORY OF HIGH TEMPERATURE MATERIALS

Prof. R. O. Suzuki: LABORATORY OF ECO-PROCESSING

#### AFFILIATE MEMBERS

Prof. K. Azumi:

Assoc. Prof. K. Fushimi:

Assoc. Prof. M. Sakairi:

Assoc. Prof. S. Hayashi:

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

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## **CURRENT ACTIVITIES and PRESENTATIONS**



## LABORATORY OF CORROSION ENGINEERING

Prof. Dr. Mikito Ueda  
TEL / FAX: +81-11-706-7813  
E mail: mikito@eng.hokudai.ac.jp  
Assist. Prof. Dr. Atsushi Hyono  
TEL +81-11-706-6354  
E mail: hyono@eng.hokudai.ac.jp

Secretary Mrs. Tamaki Hida  
TEL/FAX: +81-11-706-7813  
E-mail: thida@eng.hokudai.ac.jp

### Students

Y. Lei, J. Nunomura, S. Takahashi, T. Teshima, T. Namekata, R. Nakanishi,  
Y. Yasui, S. Shibuya, S. Honda, A. Tsuruta

Assoc. Prof. Ueda was promoted to the professor of the Laboratory of Corrosion Engineering from April 2013. Mrs. Hida is working as a secretary of the laboratory from May 2013.

Our research activities are concerned with molten salts electrolysis and surface sciences about metal surface.

Research programs in progress are as follows:

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

To develop electrorefining process of metallic Na from the used Na-S battery. There is no electrorefining process of sodium in the industrial scale. We were investigated NaTFSI-TBATFSI ionic liquid as candidate of the electrolytic melt. In the electrorefining experiment for 20 hours, more than 99.9% pure Na was obtained from simulated Na in used Na-S battery.

(2) Electrodeposition of Zr in chloride-fluoride molten salt

Metallic Zr was electrodeposited on Cu substrate in LiCl-KCl-LiF molten salt containing ZrF<sub>4</sub> at 973 K. In voltammogram, cathodic current which corresponds

to reduction reactions of  $\text{Zr(IV)} + 2e \rightarrow \text{Zr(II)}$  and  $\text{Zr(II)} + 2e \rightarrow \text{Zr(0)}$  were flowed at -1.4 and -1.6 V vs.  $\text{Ag/Ag}^+$ , respectively. The electrodeposition was performed by constant potential electrolysis from -1.4 to -1.6 V. The Zr was electrodeposited as a  $\text{Cu}_{10}\text{Zr}_7$  and CuZr on Cu substrate at -1.6 V.

### (3) Electrodeposition of Al-Sn alloy in chloride-fluoride molten salt

The Al-Sn alloys were electrodeposited in an  $\text{AlCl}_3$ -NaCl-KCl molten salt containing  $\text{SnCl}_2$  at 423 K. Reduction of the Sn ions started at a potential of 0.5 V vs. Al/Al(III) in the molten salt. Co-deposition of Al and Sn occurred at potentials more negative than 0.1 V. The ratio of the Sn in the electrodeposits decreased with the potential from 100 at.% at 0.2 V to 19 at.% at -0.3 V.

### (4) Development of Al-Cl<sub>2</sub> cell in ionic liquid

To develop an aluminum-chlorine cell, an electrochemical cell consisting of an aluminum anode and a graphite cathode was developed and evaluated in EMIC- $\text{AlCl}_3$  ionic liquid.

The relationship between current density and cell voltage in the cell showed an almost linear relation. The output characteristics of the cell depend on the configuration of the graphite cathode, the current density with a step type cathode at 0.5 V was about 20 % better than that of a cylindrical type graphite cathode.

### (5) Development of efficient PEFC cathode for oxygen reduction reaction (ORR)

Oxygen reduction reaction (ORR) was studied on Pd electrodes. The Pd electrode did not reveal a high ORR current and when it was covered by mono-atomic layers of Pt, however, the ORR current compared to that of Pt electrode.

The ORR current was also examined by a co-deposition layer of Co and Pt on carbon electrode. Co was firstly electrodeposited on the electrode and then the electrodes was immersed in the acidic solution containing Pt ions. The Co layer was replaced with Pt in atomic level. The surface layers containing Co and Pt thus formed exhibits a relative high ORR current.

### (6) Investigation of Li metal surface by in situ Raman spectroscopy

Li metals in some non-aqueous solution were evaluated by Raman spectrometer. Some compounds by oxidized of Li were identified.

Other Activities:

Prof. Ueda attended the 19<sup>th</sup> International Vacuum Congress, Paris, France, September 9-13, 2013 and presented paper entitled by "Electroplating of Al on Mg alloys in an ionic liquid for corrosion protection".

## Presentations

H. Saito, A. Hyono, M. Ueda, T. Ohtsuka, In situ Raman spectroscopy of Li electrodes surface in electrolyte. Winter Joint Meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 24-25, 2013

M. Sasaki, A. Hyono, M. Ueda, T. Ohtsuka, Corrosion protection of steel covered with conducting polypyrrole doped with heteropoly molybdate ions, Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 29-30, 2013

R. Inaba, A. Hyono, M. Ueda, T. Ohtsuka, Effect of electrolysis current density for Na electrorefining in NaTFSI-TBATFSI ionic liquid, Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 29-30, 2013

C. Namekata, A. Hyono, M. Ueda, T. Ohtsuka, Al electrodeposition by constant current and pulse electrolysis in  $\text{AlCl}_3$ -EMIC ionic liquid, Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 29-30, 2013

A. Hyono, H. Saito, M. Ueda, T. Ohtsuka, In situ Raman spectroscopy for the lithium electrodes surface in organic solution, Seventh International conference on Molecular Electronics and Bioelectronics (M&BE7), Fukuoka, March 17-19, 2013

R. Inaba, M. Ueda, T. Ohtsuka, Electrorefining reaction of Na in NaTFSI – TBATFSI ionic liquid, 80th time of ECSJ, Tohoku University, Sendai, March 29-31, 2013

J. Nunomur, M. Ueda, T. Ohtsuka, Effect of circular cone shape cathode for reduction reaction of  $\text{Cl}_2$  in EMIC –  $\text{AlCl}_3$  ionic liquid, 80th time of ECSJ, Tohoku University, Sendai, March 29-31, 2013

M. Ueda, Electroplating of Al alloys in non-aqueous solution, AIST

materials processing meeting, Sapporo, June 13, 2013

R. Nakanishi, M. Ueda, T. Ohtsuka, In-situ observation of growth process of Al electroplating in EMIC-AlCl<sub>3</sub> ionic liquids, the 29th Lilac seminar and the 19th research exchange meeting for young researchers, Otaru, June 15-16, 2013

T. Teshima, M. Ueda, T. Ohtsuka, Electrodeposition of Al-Zr alloys in chloride molten salts containing supersaturated ZrCl<sub>4</sub>, the 29th Lilac seminar and the 19th research exchange meeting for young researchers, Otaru, June 15-16, 2013

M. Ueda, Development of Al-Cl<sub>2</sub> cell in molten salts or ionic liquids, the 181st meeting of molten salt committee, Fuji June 20, 2013

R. Nakanishi, M. Ueda, T. Ohtsuka, In-situ observation of growth process of Al electroplating in EMIC-AlCl<sub>3</sub> ionic liquids, Summer meeting 2013 of Hokkaido branch of The Chemical Society of Japan, Kitami, July 20, 2013

C. Namekata, M. Ueda, T. Ohtsuka, Al electroplating by pulse electrolysis in EMIC-AlCl<sub>3</sub> ionic liquid, Summer meeting 2013 of Hokkaido branch of The Chemical Society of Japan, Kitami, July 20, 2013

Mikito Ueda, Production of high purity Na by electrorefining from used Na-S secondary battery, 2013 Annual meeting of The mining and materials processing institute of Japan, Sapporo, September 3-5, 2013

Mikito Ueda, Shizuka Hariyama, Yasushi Tabei, Toshiaki Ohtsuka, Electroplating of Al on Mg alloys in an ionic liquid for corrosion protection, 19th International Vacuum Congress(IVC-19), Sep.9-13, 2013, Paris

Yuto Yasui, Mikito Ueda, Toshiaki Ohtsuka, Hitomitsu Date, Takahashi Fujii, Al electroplating on steel in EMIC-AlCl<sub>3</sub> ionic liquid, The 128th Meeting of The Surface Finishing Society, Fukuoka, September 24-25, 2013

Syunki Takahashi, Atsushi Hyono, Mikito Ueda, Toshiaki Ohtsuka, Evaluation of Pd electrodes covered with Pt monolayers, Meeting of ECSJ 2013, Tokyo, September 27-28, 2013

Atsushi Hyono, Hikari Saito, Mikito Ueda, Toshiaki Ohtsuka, Investigation of

lithium metal surfaces by in situ Raman spectroscopy, Meeting of ECSJ 2013, Tokyo, September 27-28, 2013

Tsubasa Teshima, Mikito Ueda, Toshiaki Ohtsuka, Electrodeposition of Al-Zr alloys in chloride molten salts containing Zr ion, The 45th Symposium on Molten Salt Chemistry, Yokohama, November 20-21, 2013

Junji Nunomura, Atsushi Hyouno, Mikito Ueda, Toshiaki Ohtsuka, Anodic dissolution characteristics of aluminum alloys in Al-Cl<sub>2</sub> cell, The 45th Symposium on Molten Salt Chemistry, Yokohama, November 20-21, 2013

## **Facilities and Capabilities**

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light and null-method ellipsometer for multiple-angle-of-incidence measurement

Potential Modulation Reflectance: Wavelength region from 350 to 800 nm

Raman Scattering Spectrometer: Bonko Keiki, single type of spectrometer equipped by 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

Carl Fischer moisture measuring system: Metrohm 852 titrando

Evaporator: Eyela SB1100

Electrochemistry apparatuses

Optical Microscopy

Electrochemical Corrosion Rate Monitor System

Molten salt ion-exchange apparatus for glass

Luminescence apparatus for thin surface layer equipped with He-Cd UV laser



## 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  
Assist. Prof. Etsushi Tsuji  
TEL./FAX: +81-11-706-6736  
e-tsuji@eng.hokudai.ac.jp

### Visiting Professor

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

### Students

Y. Konno, K. Shazad, H. Takano, H. Ogata, H. Oba, K. Kure, H. Sato,  
K. Nakayama, N. Hirata, F. Kataoka, K. Kikutani, T. Kimura, C. Kura,  
T. Yamasaki

The research activities of the laboratory are directed towards the development of advanced oxide films and nanomaterials utilizing anodizing process and sol-gel process for possible applications including novel fuel cells, air batteries, photovoltaic cells, corrosion protection, self-cleaning surfaces and capacitors. 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 and conversion, corrosion, passivation and surface finishing.

Current topics on research are as follows:

(1) Intermediate-temperature fuel cells

We successfully fabricated gas-tight silicate and phosphate nanofilms, which show efficient proton conductivity even in dry atmosphere at intermediate

temperatures (200-400°C). Utilizing the proton-conducting nanofilms as an electrolyte membrane, we designed a hydrogen membrane fuel cells (HMFCs). In HMFCs, palladium foil was used as a hydrogen-permeable anode and we succeeded power generation. We also found that the  $\text{ZrO}_2\text{-WO}_3\text{-SiO}_2$  films formed by anodizing of magnetron-sputtered Zr-W-Si alloys reveal high proton conductivity even below 200°C.

#### (2) Tailoring of self-organized porous anodic oxides on various 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 titanium, niobium and aluminum in the hot phosphate-glycerol electrolyte. For titanium, we succeeded to obtain mesoporous crystalline anatase films without post annealing. In addition, using organic electrolytes containing fluoride ions, self-organized nanoporous anodic films have been successfully developed on iron and stainless steel. The growth behavior and their properties have been examined in detail.

#### (3) Fabrication of superhydrophobic and superoleophobic surfaces

One of the important factors to control the surface wettability of solid materials is surface geometry. Hierarchical porous surface morphology is of particular importance to obtain superhydrophobic surfaces together with surface energy of solid materials. Further precise control of the surface geometry resulted in the formation of superoleophobic surfaces, on which oil droplets were readily rolled off. Utilizing porous anodic films, we developed hierarchical surfaces on aluminum and aluminum alloys and obtained superoleophobic surfaces after coating with a fluoroalkyl monolayer, which had the lowest surface energy.

#### (4) Novel dielectric films formed by anodizing

One of the important practical applications of the anodic films on valve metals is dielectric in electrolytic capacitors. We have examined dielectric properties of the anodic films formed on a range of novel valve metal alloys. Detailed investigations on the significant enhancement of capacitance by forming nanocomposite anodic films, consisting of nanocrystalline tetragonal  $\text{ZrO}_2$  phase and an amorphous matrix, have been conducted.

#### Other Activities:

Prof. H. Habazaki presented invited lectures at the 2013 International Symposium

on Advanced Capacitors, which was held on 27-30 May 2013 at Consomosquare Hotel and Congress, Osaka and at 1st Int. Conf. on Surface Engineering (ICSE2013) on 18-21 November 2013 at Haeundae Grand hotel, Busan, Korea. Prof. Y. Aoki presented invited lecture at the 7th International Conference on Science and Technology of Advanced Ceramics held on 6-9 June 2013 at MelPalk Hotel, Yokohama.

## Presentations

H. Habazaki, K. Ye, Y. Aoki, E. Tsuji, S. Nagata, "High proton conductivity of amorphous  $ZrO_2$ - $WO_3$ - $SiO_2$  nanofilms at intermediate temperatures", 19th International Conference on Solid State Ionics, June 2-7, Kyoto International Conference Center, Kyoto, 2013.

Y. Aoki, R. Nonaka, E. Tsuji, H. Habazaki, "Characterization of amorphous zirconium phosphate thin film base HMFC", 19th International Conference on Solid State Ionics, June 2-7, Kyoto International Conference Center, Kyoto, 2013.

K. Kikutani, Y. Aoki, E. Tsuji and H. Habazaki, "Defect thermodynamics of high valence state CrV compounds,  $Ca_5(CrO_4)_3O_{0.5}$ ", 19th International Conference on Solid State Ionics, June 2-7, Kyoto International Conference Center, Kyoto, 2013.

C. Kura, Y. Aoki, E. Tsuji, and H. Habazaki, "Resistive switching behavior of amorphous  $tiox$  thin films prepared by reactive sputtering process", 19th International Conference on Solid State Ionics, June 2-7, Kyoto International Conference Center, Kyoto, 2013.

E. Tsuji, K. Fukami, H. Habazaki, "Porosification of semiconductor electrodes by electrochemical processes under dynamic self-organization", The 4 International Symposium of Advanced Energy Science, Sept. 30-Oct. 2, Kyoto, Japan, 2013.

E. Tsuji, Y. Taguchi, Y. Aoki, H. Habazaki, "Structure Control of Mesoporous Anodic Crystalline  $TiO_2$  Films By Changing Basicity of Hot Phosphate/Glycerol Electrolytes", 224th ECS Meeting, Oct. 27-Nov. 1, Hilton San Francisco, San Francisco, USA, 2013.

H. Habazaki, H. Sato, E. Tsuji, Y. Aoki, K. Shimizu, “Characterization of Self-Assembled Monolayer On Anodized Aluminum By XPS, AFM and Low-Voltage SEM”, 224th ECS Meeting, Oct. 27-Nov. 1, Hilton San Francisco, San Francisco, USA, 2013.

Y. Konno, E. Tsuji, Y. Aoki, T. Ohtsuka, H. Habazaki, “Formation of Composite Coatings of Porous Anodic Oxide/ Polypyrrole for Corrosion Protection on Steels”, The 2nd International Symposium of Frontier Chemistry Center –Advanced Materials Science–, 9-10, December, Hokkaido Univ., Sapporo, 2013.

K. Kure, E. Tsuji, Y. Aoki, H. Habazaki, “Fabrication of hierarchical stainless steel surfaces for super-liquid repellency”, Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. –Guangxi Univ. Joint Symposium —Materials Science and Nanotechnology for the 21th Century—, 11-13 December, Guangxi University, Nanning, China, 2013.

## **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 and PT-X, suitable for the preparation of electron transparent TEM sections.

AFM: SII SPA-400 system with conductive AFM mode as well as contact and tapping modes.

Impedance analyzer: Solartron 1260, measureable in the frequency range of 10  $\mu$ Hz 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  
Assoc. Prof. Dr. Lihua Zhang  
Tel+81-11-706-6844, Fax+811-11-706-7119  
E-mail : zhanglihua@eng.hokudai.ac.jp

### Technical Staffs

Mr. Jyun-ichi Tanaka  
Mr. Shin-ichi Kojima  
Ms. Masako Ogura

### Students

F. Sakota, T. Kanaya, A. Kawanami, R. Fukabori

Research work at “Laboratory of high temperature materials” directs toward 1) high-temperature corrosion of SiO<sub>2</sub>-forming materials, 2) oxidation of Fe-Si steels in N<sub>2</sub>-H<sub>2</sub> atmospheres, 3) high temperature oxidation of metal disilicides, and 4) physical and mechanical properties of SiAlON-metal composites. Assoc. Prof. Dr. Zhang from China joined our laboratory from August. She is now studying high-temperature oxidation corrosion of various composites.

Current topics on research are as follows:

#### (1) High-temperature corrosion of SiO<sub>2</sub>-forming alloys

High-temperature corrosion tests of Al<sub>2</sub>O<sub>3</sub>- or SiO<sub>2</sub>-forming alloys such as CoNiCrAlY and CoNiCrAlY-Si alloys in molten Na<sub>2</sub>SO<sub>4</sub> and NaCl salts and gaseous O<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub>-NaCl atmospheres are being carried out. The SiO<sub>2</sub> formers showed excellent corrosion resistance based on the selective oxidation of Si in the both atmospheres. The result demonstrates that the SiO<sub>2</sub>-forming materials completely prevent the formation of sulfide and chloride at the scale/substrate interface and the internal sulfidation and chlorination in the substrate. On the other hand, Al<sub>2</sub>O<sub>3</sub> formers could not prevent the internal sulfidation and chlorination.

(2) Annealing of high Si steels in  $N_2$ - $H_2$  atmosphere

Annealing of Fe-(0.1-1 mass%)Si steels is being carried out in  $N_2$ - $H_2$ . Based on the results, the relationship between change of surface morphology of the steels and Si content is being studied. With increasing Si content and annealing temperature, faceted iron grains were remarkably formed on the steel surface. This is caused by the formation of internal Si oxide during cooling. At present, the effects of third elements, which have higher affinity for oxygen, on the surface morphology are being studied.

(3) High temperature oxidation of  $NbSi_2$ -X(B, Ge, Al)

To improve oxidation resistance of  $NbSi_2$ , a third element such as B, Ge, and Al was added into  $NbSi_2$  and the influences of additives on the oxidation resistance were investigated. Ge and Al additions didn't lead to the formation of additional phases. Oxidation resistance of  $NbSi_2$  was remarkably improved by B, Ge, and Al additions more than 3mass%. This is due to the formation of a low viscosity silica layer in B and Ge added  $NbSi_2$  and the formation of an Al-rich oxide layer in Al-added  $NbSi_2$ . At present, the microstructure and element distribution in oxide scales formed on the substrate are being observed by TEM-EDX.

(4) Mechanical properties and high-temperature corrosion resistance of SiAlON-metal composites.

SiAlON is one of attractive materials for ultra-high temperature applications. In our laboratory, to utilize it as a coating material for boiler tubes the high temperature oxidation behavior in atmospheres containing water vapor and the high temperature corrosion behavior of SiAlON-metal composites in atmospheres containing aggressive elements such as sulfur and chlorine are being studied. In addition, improvement of mechanical properties of the composites is also being performed.

Other activities:

In March, Prof. Kurokawa and Mr. Kimura attended The 20<sup>th</sup> Inter'l Workshop on Plasma Application and Hybrid Functionally Materials in Kuala Lumpur, Malaysia, and presented a paper entitled "High temperature corrosion behavior of  $SiO_2$ -forming alloys at 923 K in the liquid phase of  $Na_2SO_4+25.7\text{mass}\%NaCl$ ". In July, Prof. Kurokawa and Mr. Kanaya attended The AGH (Poland)-Hokkaido Univ. Joint Symposium in Sapporo, Japan, and presented two papers entitled "High-Temperature Corrosion of  $SiO_2$ -Forming Materials" and "Improvement of

Oxidation Resistance of NbSi<sub>2</sub> by Addition of Al". In Sept., Prof. Kurokawa attended The 9<sup>th</sup> Inter'l Symposium on Applied Plasma Science, in Istanbul, Turkey, and presented a paper entitled "Formation of internal oxide during annealing in extremely low dew point atmosphere". In Dec., Prof. Kurokawa attended The ISO/TC156/WG13 Meeting held in Frankfurt, Germany. In Dec., Prof. Kurokawa attended The Symposium on Green Energy and Technology at IIMU in Kuala Lumpur, Malaysia.

Prof. Kurokawa is now arranging the international symposium on high temperature oxidation and corrosion 2014 (ISHOC 2014) in Hakodate, Hokkaido, as the chairman.

## Presentations

Coatings having outstanding high-temperature corrosion resistance; K. Kurokawa: Symposium at Osaka Univ., Osaka, Feb., 2013.

High temperature corrosion behavior of SiO<sub>2</sub>-forming alloys at 923 K in the liquid phase of Na<sub>2</sub>SO<sub>4</sub>+25.7mass%NaCl; T. Sudiro, S. Kyo, O. Ishibashi, M. Nakamori, and K. Kurokawa: The 20<sup>th</sup> Inter'l Workshop on Plasma Application and Hybrid Functionally Materials: in Kuala Lumpur, Malaysia, Mar., 2013.

Effects of added elements on high temperature oxidation resistance of NbSi<sub>2</sub>; M. Ukegawa, K. Kimura, T. Kanaya, and K. Kurokawa: Spring Meeting of Jpn. Inst. Met., Tokyo, Mar., 2013.

High-Temperature Corrosion of SiO<sub>2</sub>-Forming Materials; K. Kurokawa: The AGH-Hokkaido Univ. Joint Symposium, Sapporo, July, 2013.

Improvement of Oxidation Resistance of NbSi<sub>2</sub> by Addition of Al; T. Kanaya and K. Kurokawa: *ibid.*

Formation of internal oxide during annealing of Fe-Si alloy in extremely low dew point atmosphere; F. Sakoda and K. Kurokawa: The 6<sup>th</sup> Inter'l Symposium on Plasma Application and Hybrid Functionally Materials, Kuala Lumpur, Malaysia, 2013.

Formation of internal oxide during annealing in extremely low dew point

atmosphere; F. Sakoda and K. Kurokawa: The 9<sup>th</sup> Inter'l Symposium on Applied Plasma Science, Istanbul, Turkey, Sept., 2013.

High-temperature corrosion of boiler tube -Difference between air and oxygen combustion manners-; J. Tanaka, K. Kurokawa, K. Goto, and Y. Matsunaga: Fall Meeting of Jpn. Inst. Met., Kanazawa, Sept., 2013

Sintering behavior of nanosize powders of WC; A. K. Nanda Kumar, M. Watabe and K. Kurokawa: The 18<sup>th</sup> Workshop on Sintering, Sendai, Nov., 2013.

## **Facilities and Capabilities**

Spark Plasma Sintering Equipment

Ultra-High Vacuum Furnace with Mass Spectrometer

Oxidation Test Equipment with Thermobalance and Ultra-High Temperature Furnace

Micro-Thermobalance

Acoustic Emission system

Differential Scanning calorimeter

Scanning Electron Microscopy

Micro Vickers Hardness Tester

Optical Microscope with High-Temperature Furnace



## **ECO-PROCESSING LABORATORY**

Prof. Dr. R. O. Suzuki

Tel.:+81-11-706-6339 Fax.:+81-11-706-7882

E-mail:rsuzuki@eng.hokudai.ac.jp

Assoc.Prof. Dr. T. Kikuchi

Tel.:+81-11-706-6340 Fax.:+81-11-706-6341

E-mail:kiku@eng.hokudai.ac.jp

Research Assoc. Dr. S. Natsui

Tel.:+81-11-706-6340 Fax.:+81-11-706-6342

Tech. Staff, Ms. M. Kitamura, Mr. H. Noguchi, Ms. A. Yamase

Tel.:+81-11-706-6339 Fax.:+81-11-706-7882

E-mail:m-kitsmura@eng.hokudai.ac.jp, noguchihiro@eng.hokudai.ac.jp,  
yamase@eng.hokudai.ac.jp

### **Foreign Researchers**

Xiang Ning MENG

### **Students**

M. Baba, M. Yoshida, A. Sado, T. Yamamoto, T. Uchiyama,  
K. O. Ito, O. Nishinaga, R. Ishida, T. Wakamatsu,  
J. Kawashima, H. Takai, D. Nakajima, H. Hada, F. Matsuura

Prof. Ryosuke O. Suzuki merged as the professor of the laboratory of Eco-processing from Kyoto University on March 2006. He studies the non-ferrous metallurgy based on the molten salt electrolysis. His research activities are directed to design the economical and environment-friendly processes for materials production at high temperatures. The extraction metallurgy of the refractory metals such as Nb and Ta, and of valve metals such as Ti, V and Zr, serves many topics when the electrolysis of CaO in the molten CaCl<sub>2</sub> is applied. The electrolysis of CO<sub>2</sub> gas is one of the extreme cases in oxide decomposition. The thermoelectric power generation is designed from the view of material design and heat exchange.

Dr. Kikuchi joined as an associate professor from laboratory of interface microstructure analysis on May 2010, and he began to study the micro- and nano-structure fabrication by electrochemical techniques such as anodizing, electrochemical etching, and electrodeposition. Electroless calcium reduction of titanium, zirconium, neodymium, and iron oxides in calcium chloride molten salt at high temperature was also investigated for novel electronic device fabrication and recycling of these metals.

Dr. Natsui joined as an assistant professor from Tohoku University on April 2013. His research activities are directed to design the low-carbon ferrous metallurgy by using current numerical simulation technology such as discrete element method, its coupling to CFD, and particle based hydrodynamics. And he began to study the high-efficiency technology of CO<sub>2</sub> gas decomposition process by coupling of electrochemical analysis and in-situ observation of high-temperature molten salt electrolysis.

Current topics on corrosion research are in the following:

(1) Molten salt electrolysis of CaCl<sub>2</sub>

Reduction of the oxides of Ti, Nb and Ta are studied, when the CaO dissolved in the molten CaCl<sub>2</sub> is electrochemically decomposed to form metallic calcium. A low oxygen potential produces the metallic powders at the cathode. The reduced metallic powder is prepared directly from the oxides. The mechanism of this proposal is examined from the electrochemistry and thermodynamics. CO<sub>2</sub> gas reduction catches the current interests in the morphology of precipitated carbon particles.

(2) Micro- and Nano-structure fabrication by anodizing

Anodic porous alumina has been widely investigated and used as a nanostructure template in various nano-applications. The nano-morphology of porous alumina is limited by the narrow range of electrolyte species used for anodizing. Therefore, the discovery of additional electrolytes would greatly expand the applicability of porous alumina. Very recently, we have been working on new electrolytes for anodic porous alumina, such as selenic (H<sub>2</sub>SeO<sub>4</sub>), squaric (3,4-dihydroxy-3-cyclobutene-1,2-dione), and

acetylenedicarboxylic ( $\text{HOOC-C}\equiv\text{C-COOH}$ ) acids. Our novel anodic porous alumina can be used as a nanotemplate for various nanostructures in 100-, 10-, and sub-10-nm-scale manufacturing.

### (3) Low-carbon ferrous metallurgical design

In a ferrous metallurgical process, multiphase flow plays an important role in increasing the efficiency by stirring liquid mechanically or by injecting a gas. Owing to the difficulty of direct observation in a high-temperature system or real furnace experiment, numerical analysis is useful and studied. We presents a new particle-based simulation scheme for gas-liquid flow. We improved the numerical stability, which is generally a problem with the particle method, and verified the model's accuracy for fundamental gas-liquid flow analysis. This scheme is also applicable to phenomena in an actual process that includes many dispersal phases.

Other activities:

### (4) Thermoelectric power generation

An optimization of the thermoelectric generation is mathematically designed for the highest output. This work links with energy harvesting to conduct the electrolysis. The utilization of solar energy is challenged using cheap materials such as water.

Prof. R.O. Suzuki organized 4th Intern. Workshop on Thermoelectrics, 4-6 July 2013 at Awaji Island.

The following foreign scientist visited this laboratory : Prof. A. Wiedenkauff (Switzerland), Prof. J. Snyder (USA), and Prof. L. Rosendhal (Denmark). Dr. Xiangning Meng, Northeastern University, China, joined in our group as JSPS postdoctoral fellow on August 2012 for 2-years project.

## **Presentations**

Development of silicide thermoelectric material and module; R. Funahashi, Y. Masumura, R.O. Suzuki, S. Katsuyama, T. Takeuchi and E. Combe : The Materials Research Society Fall Meeting, 1-6 Dec., 2013, Hynes Convention Center, Boston, Massachusetts, USA.

Various proposals on refining of metallic titanium; R.O. Suzuki : Light Metal Soc., Tohoku regional meeting, 22 Nov., 2013, Tohoku Univ., Sendai, Japan.

Decomposition of CO<sub>2</sub> by molten salt electrolysis in CaCl<sub>2</sub>-CaO; T. Uchiyama, T. Wakamatsu, S. Natsui, N. Sakaguchi, T. Kikuchi and R.O. Suzuki: 45th Symposium on Molten Salt Chemistry, 20-21 Nov., 2013, Keio Univ., Yokohama, Japan.

Decomposition of CO<sub>2</sub> by molten salt electrolysis in LiCl-Li<sub>2</sub>CO<sub>3</sub>; T. Wakamatsu, T. Uchiyama, M. Kitamura, S. Natsui, T. Kikuchi and R.O. Suzuki : *ibid.*

Numerical analysis of molten salt flow using 3-dimensional multi-phase particle method; S. Natsui, H. Takai, T. Kikuchi and R.O. Suzuki: *ibid.*

Anodizing of aluminum with meltdrum's acid; A. Sado, T. Kikuchi, S. Natsui, and R. O. Suzuki : The 30<sup>th</sup> Anodizing Research Society Conference, Hirosaki, Japan, Nov., 2013.

Growth behavior of anodic oxide films formed by anodizing in squaric acid; T. Yamamoto, T. Kikuchi, S. Natsui, and R. O. Suzuki : *ibid.*

Fabrication of porous titanium via calciothermic reduction of titania nano-particles; M. Yoshida, T. Kikuchi, S. Natsui, H. Habazaki, and R. O. Suzuki : *ibid.*

Effect of concentration of selenic acid on the regularity of anodic porous alumina; O. Nishinaga, T. Kikuchi, S. Natsui, and R. O. Suzuki : *ibid.*

Findings of novel anodic porous alumina; T. Kikuchi : *ibid.*

Optimization of Module Shape in Thermoelectric Power Generation; R.O. Suzuki and T. Fujisaka : 2nd International Symposium on Inorganic and Environmental Materials, 27-31 Oct., 2013, Universite de Rennes 1, Rennes, France.

A light-concentration characteristic of the water lens and its application to the thermoelectric generation; K. O. Ito, H. Sui, X. Meng and R.O. Suzuki : *ibid.*

Thermoelectric analysis for a three-dimensional power generation system in helical; X. Meng, T. Fujisaka, K. O. Ito and R.O. Suzuki : *ibid.*

Decomposition of Carbon Dioxide by  $\text{CaCl}_2\text{-CaO}$  molten salt electrolysis; T. Uchiyama, T. Wakamatsu, S. Natsui, N. Sakaguchi, T. Kikuchi and R.O. Suzuki : International Conference on Smart Carbon Saving and Recycling for Ironmaking (ICSRI), 2-4 Oct., 2013 Hayama, Kanagawa, Japan.

$\text{CO}_2$  decomposition by electrolysis in  $\text{LiCl-Li}_2\text{CO}_3$  molten salt; T. Wakamatsu, T. Uchiyama, T. Kikuchi and R.O. Suzuki : *ibid.*

Formation of high-crystallinity carbon by reduction of carbon dioxide; T. Kikuchi, H. Nishiyama, R. Ishida, T. Uchiyama, T. Wakamatsu, S. Natsui, N. Sakaguchi, and R. O. Suzuki : The 128<sup>th</sup> Annual Meeting of Surf. Finish. Soc. Jpn., Fukuoka, Japan, Sep., 2013.

Novel highly ordered nano-porous alumina by selenic acid anodizing; O. Nishinaga, T. Kikuchi, and R. O. Suzuki : *ibid.*

Fabrication of nano-porous alumina by squaric acid anodizing; T. Yamamoto, T. Kikuchi, S. Natsui, and R. O. Suzuki : *ibid.*

Growth behavior of nanotubes formed by anodizing of titanium; A. Sado, T. Kikuchi, S. Natsui, and R. O. Suzuki : *ibid.*

Thermoelectric Analysis for  $\Pi$ -type Module with Tilted Elements; X. Meng, T. Fujisaka, K. O. Ito and R. O. Suzuki : IUMRS-ICAM2013 International Conference on Advanced Materials, 22-28 Sept., 2013, Qingdao International Convention Center, Qingdao, China.

$\text{CO}_2$  dissolution and its decomposition in  $\text{LiCl-Li}_2\text{O}$  melt; T. Wakamatsu, T. Uchiyama, S. Natsui, T. Kikuchi and R.O. Suzuki: 153rd Annual Meeting of Japan Institute of Metals (Fall session), 17-19 Sept., 2013, Kanazawa Univ., Kanazawa, Ishikawa, Japan.

Fabrication of porous titanium by reduction of titania nano-particles with calcium reductant; M. Yoshida, T. Kikuchi, S. Natsui, H. Habazaki, and R. O. Suzuki : *ibid.*

Reduction behavior of zirconia nano-particles during calciothermic reduction; R. Ishida, T. Kikuchi, and R. O. Suzuki : *ibid.*

CO<sub>2</sub> decomposition using CaCl<sub>2</sub> melt and ZrO<sub>2</sub> solid electrolyte; T. Uchiyama, T. Wakamatsu, S. Natsui, N. Sakaguchi, T. Kikuchi and R.O. Suzuki: 166th Annual Meeting of Iron and Steel Institute of Metals (Fall session), 17-19 Sept., 2013, Kanazawa Univ., Kanazawa, Ishikawa, Japan.

Basic Study of Numerical Analysis of Gas-Liquid Flow using Particle Method Simulation; S. Natsui, H. Takai, T. Kikuchi, R. O. Suzuki: *ibid.*

Simulation of Thermoelectric Module with Parallelogram Elements; X. Meng, T. Fujisaka, K.O. Ito and R.O. Suzuki : 10th Annual Meeting of Thermoelectric Society of Japan, 8-9 Sept., 2013, Nagoya Univ., Nagoya, Aichi, Japan.

Water lens for application of solar thermoelectric generation; K.O. Ito, H. Hakozaki, H. Kinoshita and R.O. Suzuki : *ibid.*

CO<sub>2</sub> decomposition by using molten salt and solid state electrolyte; R.O. Suzuki, T. Wakamatsu, T. Uchiyama and T. Kikuchi : Annual meeting of mining and materials processing institute of Japan, Fall session, 3-5 Sept., 2013, Hokkaido Univ., Sapporo, Hokkaido, Japan.

Micro- and nano-technologies of porous anodic oxides; T. Kikuchi : 2013 Fall Meeting of the Mining and Materials Processing Inst. Jpn., Sapporo, Japan, Sep, 2013.

Calciothermic reduction of zirconia micro- and nano-particles; R. Ishida, T. Kikuchi, and R. O. Suzuki : The Summer Sessions of The Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Japan, July, 2013.

Anodizing of aluminum in selenic acid solution; O. Nishinaga, T. Kikuchi, and R. O. Suzuki : *ibid.*

CO<sub>2</sub> gas dissolution into LiCl-Li<sub>2</sub>O melt; T. Wakamatsu, T. Uchiyama, T. Kikuchi and R.O. Suzuki : *ibid.*

Thermoelectric power generation using solar light concentration; K.O. Ito, H.

Hakozaki, H. Kinoshita and R.O. Suzuki : *ibid.*

CO<sub>2</sub> Gas decomposition Using ZrO<sub>2</sub> anode in Molten Salt; T. Uchiyama, T. Wakamatsu, S. Natsui, N. Sakaguchi, T. Kikuchi and R.O. Suzuki : Hokkaido University-AGH university of science and technology joint symposium 2013, 18-20 July 2013, Hokkaido University and Jozeikai Manseikaku Millione, Sapporo, Hokkaido, Japan.

Design of TE generation under a constant heat flux; R.O. Suzuki, H. Sui, T. Fujisaka, K.O. Ito and X. Meng : JST-EPSRC& CREST 4th International workshop on thermoelectrics, 4-6 July 2013, The Westin Resort & Conference Center Awaji Island, Awaji, Hyogo, Japan.

Thermoelectric analysis of a helical power generation system; X. Meng, T. Fujisaka and R.O. Suzuki : *ibid.*

Simulation of water lens to use for thermoelectric generation; K.O. Ito, H. Hakozaki, H. Kinoshita and R.O. Suzuki : *ibid.*

Optimal design of thermoelectric modules under solar radiation; R.O. Suzuki, T. Fujisaka, K.O. Ito, X. Meng and H. Sui : 32nd international conference on thermoelectrics (ICT2013), 30 June – 4 July, 2013, Kobe International Conference Center, Kobe, Japan.

Thermoelectric analysis for a helical power generation system; X. Meng, T. Fujisaka and R.O. Suzuki : *ibid.*

Light Concentration by Water Lens for Thermoelectric Generation; K.O. Ito, H. Sui and R.O. Suzuki : *ibid.*

CO<sub>2</sub> decomposition using zirconia anode and molten salt electrolysis; R.O. Suzuki, T. Uchiyama, T. Wakamatsu, M. Kitamura, K. Otake, N. Sakaguchi and T. Kikuchi : 7th Meeting of ACRES (Carbon circulated steel making) group, Institute of steel and iron making, Japan, 17-18 June, 2013, Tohoku University, Sendai, Miyagi, Japan.

Development of technology for CaTiO<sub>3</sub> refining as starting from the oxide raw material; R.O. Suzuki : Symposium on Seeking for renewal of titanium refining

technology, Titanium Society of Japan, 8 May 2013, Marunouchi-Park Building, Tokyo, Japan.

CO<sub>2</sub> decomposition using CaCl<sub>2</sub>-CaO melt and ZrO<sub>2</sub> solid electrolyte; T. Uchiyama, T. Wakamatsu, N. Sakaguchi, T. Kikuchi and R.O. Suzuki : 165th Annual Meeting of Iron and Steel Institute of Metals (Spring session), 27-29 March, 2013, Tokyo Univ. of Science, Tokyo, Japan.

Fabrication of Ti-Zr micro-porous alloy for electrolytic capacitor applications; M. Yoshida, Y. Taguchi, T. Kikuchi, H. Habazaki, R.O. Suzuki: 152nd Annual Meeting of Japan Institute of Metals, Tokyo, Japan, Mar., 2013.

Deformation Simulation of Copper Plates of Slab Continuous Casting Mold; X. Meng, W. Wang, M. Zhu and R. O. Suzuki : 142nd Annual Meeting and Exhibition (TMS2013), 4th International Symposium on High-Temperature Metallurgical Processing, 3-7 March 2013, San Antonio, Texas, USA.

Growth behavior of anodic porous alumina via malic acid anodizing at nano-morphology; T. Yamamoto, T. Kikuchi, and R. O. Suzuki : The 127<sup>th</sup> Annual Meeting of Surf. Finish. Soc. Jpn., Saitama, Japan, Mar., 2013.

Fabrication of highly ordered titania nanostructures by two-step anodizing; A. Sado, T. Kikuchi, and R. O. Suzuki : *ibid.*

Fabrication of Ti-Zr alloy with microporous structures; M. Yoshida, Y. Taguchi, T. Kikuchi, H. Habazaki, R.O. Suzuki : The Winter Joint Meeting of the Hokkaido Branch of Academic Societies of Chemistry, Sapporo, Japan, Jan., 2013.

Anodizing of aluminum in malic acid solution - Formation of dimple array with sub-micron diameter; T. Yamamoto, T. Kikuchi, and R.O. Suzuki : *ibid.*

Carbon formation from CO<sub>2</sub> gas using molten salt electrolysis; T. Uchiyama, T. Wakamatsu, K. Otake, N. Sakaguchi, T. Kikuchi and R.O. Suzuki : *ibid.*

Property evaluation of thermoelectric generation using solar heat; K.O. Ito, T. Fujisaka and R.O. Suzuki : The Winter Joint Meeting of the Hokkaido Secs. of Jpn. Inst. Metals and Iron and Steel Inst. Jpn., Muroran, Japan, Jan., 2013.



CO<sub>2</sub> gas dissolution into LiCl-Li<sub>2</sub>O melt; T. Wakamatsu, T. Uchida, K. Kikuchi and R.O. Suzuki : *ibid.*

## Facilities and Capabilities

X-ray diffractometer: 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<sub>2</sub>O<sub>3</sub> 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.

Sulfur and Carbon Analyzer: LECO CS-600. Carbon and nitrogen are converted to CO and NO gas by burning in O<sub>2</sub> gas with RF heating and they are detected by the infrared absorption method. 6mass%-0.6 mass ppm.

CO/CO<sub>2</sub> Gas Analyzer IR-400: 4 sets. Yokogawa

Gas Chromatography, Shimazu

NO/SO<sub>2</sub> 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.

Thermal Analyzers: SII EXSTAR-6000 TG/DTA. With Pt heater up to 1500C.

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



## **AFFILIATE MEMBERS**



## AFFILIATE MEMBER

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

## Students

Masaki Aomi, Ali Shaaban, Yusuke Sato, Yuuta Tsugawa, Kazunori Suetake,  
Yuto Nagai, Syouhei Yamazoe, Keishi Inoue, Hiroki Murakoshi

Our group has been investigated various research subjects related to corrosion engineering, surface finishing of metals, and development of new technologies of electrochemistry. Current topics are followings:

(1) Al coating on Mg alloy from molten salt bath.

For corrosion protection of Mg alloys Al coating on AZ91D from  $\text{AlCl}_3 : \text{NaCl} : \text{KCl}$  molten salt bath has also been explored. Our previous study clarified that the protection and activation of sample surface in individual process of coating is necessary to improve the coating quality. Zn intermediate layer pre-deposited on non-active Mg alloy substrate with aid of activation pretreatment using Cu nano-particle pre-deposition was therefore prepared prior to Al electroplating in molten salt bath. From the evaluation of coating morphology and cross-sectional observation of coating interface as a function of thickness of intermediate Zn layer, 1.5 $\mu\text{m}$  of Zn layer could protect the substrate of AZ91D alloy from molten salt bath. However, 7 $\mu\text{m}$  Zn layer was required to protect substrate of AZ31 alloy probably due to less dense nucleation sites for Zn deposition on the substrate. More effective activation for AZ31 is therefore necessary than that for AZ91D.

(2) Coupling photocurrent measurement for corroding metal in atmospheric condition

Photocurrent method is an useful electrochemical technique to investigate the semiconductor properties of corrosion products. In this method the specimen is generally immersed in electrolyte solution to apply proper electrode potential for photocurrent observation. To expand the applicability of photocurrent method to *in-situ* atmospheric corrosion, "coupling photocurrent method" was

developed and applied to hot-dip Zn-Al alloy coating corroding in wet and dry cycling test. In this method two specimens of same material are adjacently embedded in resin and connected with ionic bridge to establish ionic path on the surface. Two specimens were also connected to electric circuit to measure the coupling current between them. In the corrosion test one of two specimen was exposed to corrosion condition as dropping NaCl solution, and both of them were irradiated by light of proper photon energy for excitation of photo-carrier. In case of Zn-Al alloy coatings, n-type ZnO ( $E_{BG} = 3.2$  eV) and p-Si ( $E_{BG} = 1.1$  eV) were confirmed to be evolved during corrosion test and corresponding coupling photocurrent was observed when specimen was irradiated by UV or Vis light, respectively.

### (3) Photo-electrochemical investigation of high purity iron

Corrosion behavior of iron as a function of its purity was investigated by in-labo test as photo-electrochemical and impedance measurements, and long-term exposure test in the field. Two specimens of 99.5% and 4N iron were subjected to the test. Photo-excitation properties of iron passive film as an n-type semiconductor for both samples were almost same in their shape of quantum yield spectra and bandgap energy. From impedance spectra, however, thickness of passive film at high purity is less than that at low purity. Polarization current and passive current of 99.5% iron also tended to be larger than those of 4N iron. In the exposure test, 4N iron showed lower corrosion traces. From these results it is proposed that composition of the passive film formed on iron does not essentially depend on the purity but impurity elements in low purity iron probably induce defects in the passive film to provide electronic path for larger oxidation rate than high purity one or cause thickening passive film.

### (4) Application of water absorbable polymer electrolyte to electrochemical system

Properties of superabsorbent polymer (SAP) bead of sodium polyacrylate and its applicability to the electrochemical system as a semi-solid electrolyte was investigated. Such non-fluid electrolyte is useful for easy handling electrochemical probe. SAP beads absorbing NaCl solution at various concentration was fixed in a glass tube in which Pt-CE and Ag/AgCl RE was embedded. Electric (ionic) conductivity of SAP bead was confirmed to be almost same with that of electrolyte solutions containing monovalent cations such as KCl and KNO<sub>3</sub> from impedance measurement. Divalent cations such as Cu<sup>2+</sup> caused cross-linkage of polymer chains resulting in shrinking of polymer beads. Using electrochemical probe with SAP electrolyte and electrodes built into glass tube,

measurement of electrode potential, impedance spectra, CV and polarization of local area were successfully conducted.

(5) Electrochemical CO<sub>2</sub> reduction in hydrophobic ionic liquid

Reduction of CO<sub>2</sub> emission is a key issue to realize sustainable society in near future. Electrochemical reduction of CO<sub>2</sub> gas to methane as an energy carrier medium using renewable energy sources has been investigated. Conversion efficiency of CO<sub>2</sub> to methane in the aqueous solution can be, however, low because of side reaction of water decomposition. EMIm-TFSI (1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide) ionic liquid has hydrophobic property and capability of considerable CO<sub>2</sub> absorption and thus used as a bath for electrochemical CO<sub>2</sub> reduction. GC analysis of methane gas content in the gas phase of electrochemical cell revealed that the highest efficiency of CO<sub>2</sub> conversion to methane was obtained for ionic liquid containing ca. 5000 ppm water probably due to limited supply of water molecular to suppress the side reaction of water decomposition.

(6) Promotion of high-temperature corrosion resistive  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on Ni-50Al Alloy

The effects of pure metal coatings, including Ni, Fe and Cr, on long-term oxidation kinetics, surface morphology and structure were studied. Ni-50Al alloy and Ni-coated, Fe-coated and Cr-coated samples were pre-oxidized at 900 °C in air. They were then oxidized isothermally at 1,000 °C in air. The bare Ni-50Al alloy oxidized rapidly during the initial stage of oxidation due to the formation of  $\theta$ - Al<sub>2</sub>O<sub>3</sub>, but the oxidation rate decreased after  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> had developed. Oxidation of the Ni-coated sample was slow from the beginning of oxidation even though the  $\theta$ - Al<sub>2</sub>O<sub>3</sub> was predominated for a longer oxidation time. No  $\theta$ - Al<sub>2</sub>O<sub>3</sub> developed on the Cr and Fe-coated samples, but the oxidation rates of these samples were much faster than those of bare and Ni-coated samples. Cross-sectional images revealed that the grain size of  $\alpha$ - Al<sub>2</sub>O<sub>3</sub>, which formed on Cr and Fe-coated samples, was smaller than those of bare and Ni-coated samples. These metal coatings affected the microstructure of  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> and they showed a strong effect on the growth rate of  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> in the steady-state oxidation stage.

## Presentations

- K. Azumi: "In-situ Corrosion Monitoring of Metals for Long Life Infrastructures", NTHH Symposium, Naha, Nanning, China, Dec. 10th-12st, 2013. (Poster)
- S. Yamazoe and K. Azumi: "Microplasma Formation at a Narrow Gap of the Electrolyte Flow Path", *ibid.* (Poster)
- Y. Sato, K. Azumi: "Electrocodeposition of Al-Zn alloy coatings from Al and Zn including ionic liquid electrolyte bath", FCC symposium, Hokkaido University, Dec. 9th, 2013.
- K. Azumi, J. Yajima, Y. Nagai: "In-situ corrosion monitoring of Cu foil immersed in bentonite-contact solutions", LongTermCorr2013, 2013.10-6-10, Asahikawa. (Poster)
- Yu Hang, K. Azumi, M. Ueda: "Corrosion resistive Al coating on Mg alloy from molten salt bath", 60th Annual meeting of Japan Society of Corrosion Engineering, Fukushima, Sept.24-26, 2013.
- Y. Sato, K. Azumi: "Al-Zn plating from AlCl<sub>3</sub>-EMIC ionic liquid bath", *ibid.*
- A. Shaaban, K. Azumi, S. Hayashi: "Promotion of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Formation on Ni-Al Alloy Using Ni-Fe<sub>2</sub>O<sub>3</sub> Nano-Composite Seeding Layer", *ibid.*
- K. Azumi: "In-situ Corrosion Measurement of Metals in Various Environments", HU-AGH Joint Symposium, Hokkaido University, Sapporo, Sep. 18-20, 2013.
- Y. Sato: "Electrocodeposition of Al-Zn alloy from AlCl<sub>3</sub>-EMIC ionic liquid including Zn Complexes", *ibid.* (Poster)
- K. Azumi: "In-situ Coupling photocurrent measured for plated steels in atmospheric corrosion", EUROCORR 2013, Estoril, Portugal, Sep. 1 – 5, 2013.
- Y. Sato, K. Azumi: "Optimization of electrocodepositon of Al-Zn layer from AlCl<sub>3</sub>-ZnCl<sub>2</sub>-1-Ethyl-3-Methylimidazolium Chloride ionic liquid", *ibid.*
- T. Tsuda, K. Azumi, S. Kajiyama, S. Fujita: "Protocurrent properties of corrosion products formed on hot-dip Zn-Al alloy plated steel in wet and dry cycling test", Annual meeting of Jpn. Soc. Corrosion Engi. 2013, Tokyo, May 13-15, 2013.



T. Ohtsuka, Y. Hamaguchi, M. Sakairi, K. Fushimi, K. Azumi, Y. Sakakibara, and G. Nakayama; "Oxide Films on Nickel-base Alloys in Water at 360°C under PWR Environment", 16th Intern. Conf. Environment. Degradation of Mater. in Nuclear Power Systems - Water Reactors, Asheville, NC, USA, Aug. 11-15, 2013.

S. Yamazoe, K. Azumi: "Analysis of micro-plasma generated in liquid flow path", The 127th Annual Meeting of Surf. Finish. Soc. Jpn., March 18-19, Miyashiro 2012.

Y. Tsugawa, K. Azumi: "Evaluation of water absorbing polymer electrolyte and its applications to electrochemical system", *ibid.*

Y. Sato, K. Azumi: "Al-Zn plating on steel from  $\text{AlCl}_3\text{-ZnCl}_2\text{-EMIC}$  ionic liquid bath", *ibid.* (Poster)

Y. Nagai, K. Azumi: "Effects of Silicate film formed on electrochemical properties of Pt electrode", Winter Joint Meeting of the Hokkaido Branch of the Chemistry Related Societies, Sapporo, January 29-30, 2013.

Y. Sato, K. Azumi: "Al-Zn alloy plating from  $\text{AlCl}_3\text{-ZnCl}_2\text{-EMIC}$  ionic liquid", *ibid.*

S. Yamazoe, K. Azumi: "Properties of micro-plasma formed in liquid flow path", *ibid.*

Y. Tsugawa: "Properties and possible application of water absorbing polymer electrolyte", *ibid.*

## AFFILIATE MEMBER

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

### Students

J.-S. Lee, K. Kurauchi, Y. Takabatake, H. Ikeyama, M. Jin, K. Yanagisawa,  
Y. Yamamoto

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) Grain-dependent Passive State of Iron Single Grains in Sulfuric Acid

Passivation of single grains on a polycrystalline pure iron was investigated in sulfuric acid with a micro-capillary-cell. Passivation behavior of the iron single grains under potentiostatic polarization depended on the crystallographic orientation of a substrate iron surface. Electrochemical impedance spectroscopy and cathodic reduction of the surface passivated on single grains revealed that the charge transfer resistance and the thickness of passive films depended on the orientation and that the thicker oxide film exhibited the smaller resistivity. XPS analysis evaluated that the composition of the film varied among the surface orientations. It was suggested that the structure of the passive film depended on the orientation of the iron substrate due to different surface energy and work function on each crystallographic orientation of bcc iron.

#### (2) Corrosion Behavior of Dual-Phase Carbon Steel and Super Duplex Stainless Steel

Corrosion behavior of high-purity dual-phase carbon steel composed of only ferrite and martensite phases in 0.1 M sulfuric acid was investigated by both macro- and micro-electrochemical methods. The dual-phase steel corrodes

non-uniformly due to galvanic coupling between its microstructures as well as self-corrosion of each phase. Hydrogen evolution reaction on galvanic-coupled martensite accelerates iron dissolution reaction of ferrite, though the corrosion rate of martensite was three-times larger than that of ferrite due to the self-corrosion in the acid. Totally, ferrite phases corrode selectively and the degree of selective corrosion was about two-times larger than martensite phases.

Corrosion behavior of super duplex stainless steel (SDSS) in acidic chloride solution was also investigated electrochemically. Potentiostatic polarizations of SDSS at  $-0.377$  and  $-0.447$   $V_{SHE}$  resulted in selective dissolution of gamma- and alpha-phases, respectively, and were utilized for fabricating single-phase electrodes. Potentiodynamic polarization curve of SDSS could be calculated from those of single-phase electrodes. The higher corrosion current density and less noble corrosion potential of alpha-phase characterized by galvanic connection with gamma-phase indicated that alpha- and gamma-phases were functioned as the anode and the cathode, respectively, in the corrosion of SDSS.

### (3) Fabrication of Multichannel Microelectrode-array and Its Application

Scanning probe technique such as an SECM enables to visualize the electrochemical activity on a specimen electrode. However it is not suitable to pursue the relatively rapid reaction of the electrode such as an initiation of pitting corrosion. In order to overcome this problem, a microelectrode-array has been fabricated by MEMS technologies in collaboration with Nanotechnology Platform, Waseda University. Simultaneously, a numerical calculation of diffusion problem on the microelectrode array has been conducted.  $10 \times 10$ -channels array structure with a microelectrode diameter of  $10 \mu\text{m}$  successfully showed limiting currents flowing through 100 microelectrodes independently. Interference effect between electrodes in the array was also simulated. These results have been used to re-design the array.

### (4) *In-situ* observation of passive surface by using an ellipso-microscope

The surface of polycrystalline titanium polarized anodically in sulfuric acid was monitored using an ellipso-microscope. During dynamic polarization, patch-like bright image was seen on ellipso-microscopic view, and the brightness and image changed with increase in potential. The change in the brightness and image corresponded to growth of an anodic oxide film on the surface. An in situ monitoring using the ellipso-microscope revealed that the film formation rate was dependent on the crystallographic orientation of the substrate. Breakdown of the film induced in a solution containing bromide ions was also monitored using the

microscope. Prior to the pitting propagation, the surface was partially regressed to the null condition with flow of a slightly large anodic current. AES measurement revealed that the formation of bromo-oxide resulted in localized film degradation followed by pitting corrosion.

#### (5) Convection-dependent Hydrogen Permeation into a Carbon Steel Sheet

In order to avoid hydrogen embrittlement of carbon steel sheet, basic research for mechanism and kinetics of hydrogen penetration is necessary. The Devanathan-Stachurski electrochemical cell for measurement of hydrogen-permeation into a steel sheet was extended to an electrolyte-flowing design. Increase in flow rate of the entry cell induces increase in hydrogen-evolution current at the entry electrode but decrease in hydrogen-permeation current at the hydrogen-exit electrode. Hydrogen-permeation is actualized by a sinusoidal perturbation of the entry-flow rate. The hydrogen-permeation response, i.e., phase shift of the detection current from the evolution current, was proportional to the square root of flow rate frequency and was dependent on sheet thickness. The sinusoidal perturbation of entry-flow rate is a new factor influencing hydrogen-permeation into the sheet.

#### Other Activities

In June, Mr. Yu Takabatake attended to 9th International Symposium on Electrochemical Impedance Spectroscopy (EIS2013), Ginowan, Japan and presented the paper entitled "Grain-dependent Passive Oxide Film Formed on Iron in Sulphate Solution". In September, Dr. Koji Fushimi attended to Eurocorr2013, Estoril, Portugal, and presented the paper entitled "Bromide ions-degradation of anodic oxide film on titanium observed by ellipso-microscopy". In November, Dr. K. Fushimi attended NACE East Asia And Pacific Rim Area Conference 2013, Kyoto, Japan and presented the keynote lecture entitled "Ellipso-microscopic imaging of passivated titanium surface".

## Presentations

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa; Grain-dependent Passive Oxide Film Formed on Iron in Sulphate Solution, 9th International Symposium on Electrochemical Impedance Spectroscopy (EIS2013), Okinawa Convention Center and Laguna Garden Hotel, Ginowan, June 16-21, 2013.

A. Kawashima, T. Nakanishi, K. Fushimi, Y. Hasegawa; In-situ observation of EuS aggregations using luminescent naphthalene units, 14th Chitose International Forum on Photonics and Technology, Chitose Institute of Science and Technology, Chitose, July 8-9, 2013.

Y. Hirai, T. Nakanishi, K. Fushimi, Y. Hasegawa; Synthesis and photophysical properties of supramolecular Eu(III) complex, 14th Chitose International Forum on Photonics and Technology, Chitose Institute of Science and Technology, Chitose, July 8-9, 2013.

T. Ohtsuka, Y. Hamaguchi, M. Sakairi, K. Fushimi, K. Azumi, Y. Sakakibara, G. Nakayama; Oxide Films on Nickel-base Alloys in Water at 360 °C under PWR Environment, 16th International Conference on Environmental Degradation of Materials in Nuclear Power Systems- Water Reactors, The Grove Park Inn, Asheville, NC, USA, August 11-15, 2013.

K. Fushimi, K. Kurauchi, T. Nakanishi, Y. Hasegawa, T. Ohtsuka; Bromide ions-degradation of anodic oxide film on titanium observed by ellipso-microscopy, Eurocorr2013, Estoril, Portugal, September 1-5, 2013.

K. Fushimi, K. Kurauchi, T. Nakanishi, Y. Hasegawa, T. Ohtsuka; Ellipso-microscopic imaging of passivated titanium surface, NACE East Asia And Pacific Rim Area Conference 2013, Kyoto International Conference Center, Kyoto, November 19-21, 2013.

## **AFFILIATE MEMBER**

Assoc. Prof. Dr. M. Sakairi  
Tel.:+81-11-706-7111, Fax.:+81-11-706-7881  
E-mail: msakairi@eng.hokudai.ac.jp

## **Postdoctoral researcher**

Dr. S. Ningshen  
Tel.:+81-11-706-7112, Fax.:+81-11-706-7881  
E-mail: sningshen@gmail.com

## **Students**

S. Takagi, T. Sasaki, T. Yamaguchi, R. Sasaki, K. Igarashi, H. Mizukami, M. Matsutomo and V. Goyal

Dr. Ningshen has finished staying our group as JSPS research fellow and returned to Corrosion Science and Technology Group, Indira Gandhi Centre for Atomic Research, India. Mr. Varitant Goyal, Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, India, joined our group as internship student from 10, May 2013 to 13th July 2013.

Research work of our group directs toward 1) Corrosion behavior of metals in nuclear reprocessing plant environments, 2) Porous type anodic film formed at selected area by solution flow type micro-droplet cell and its application, 3) permeated hydrogen formed during corrosion detected by micro electrochemical technique, 4) effect of metal cations on passive film structure of aluminum alloys in model tap water, 5) effect of  $\text{CH}_3\text{COONa}$  concentration on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments, 6) formation of hydrophobic porous alumina films on aluminum alloy by desiccation treatment and the corrosion resistance, 7) formation of composite oxide films for dielectric materials by anodizing and LPD, 8) multi layer structure of Cu-Ni with nano-size thickness formation and its property, 9) Field exposer test in cold and heavy snow district.

The topics of investigation are in the following:

(1) Corrosion behavior of metals in nuclear reprocessing plant environments

The corrosion degradation of materials in high concentration of nitric acid for nuclear fuel reprocessing plants is significant issues, and corrosion research plays an important role as a basic technology to support the reliability of a PUREX reprocessing plant. For this demands plant constructed to a high standard of integrity with excellent corrosion-resistant materials, therefore, the present research work focuses on corrosion issues of newer materials for spent nuclear fuel reprocessing plant application. The outcome of the present research work has provided insights about the corrosion reliability of new 9% Cr - 15 %Cr oxide dispersion strengthen (OSD) steels. The basic corrosion mechanism fundamental and comparative high-temperature corrosion studies of ODS alloys with pure Ti, Ti alloys (KS50AKOT), and AISI type 304L stainless has been investigated in the current work.

(2) Porous type anodic film formed at selected area by solution flow type micro-droplet cell and its application

The porous type anodic oxide films are widely used and studied, because there highly ordered pore structure. However, almost all research on area-selected anodizing is carried out with mask-processes. The solution flow type micro-droplet cell (Sf-MDC) has been applied to form thick porous type aluminum anodic oxide film at selected area. It is possible to reduce the width of the formed anodic oxide line without changes in the film formation reaction by side wall coated Pt wire electrode. Up to ten repeated passes, there is no change in the oxide film growth rate; the width of the oxide lines was observed by a coated Sf-MDC electrode. Moreover, this technique can form 110  $\mu\text{m}$  thickness porous type anodic oxide film at selected area.

(3) Permeated hydrogen formed during corrosion detected by micro electrochemical technique and Laser irradiation

The recent demand for reducing the automotive weight to improve fuel efficiency requires high strength steels. It is, however, difficult to use very high strength steels in practice because of the high susceptibility to hydrogen embrittlement. The Laser irradiation and micro electrochemical detection to detect permeated hydrogen was applied to investigate effect of area size of model scratch formed on Zn and Zn-Al coated layer on generation of hydrogen. During wet/dry corrosion tests, there is no increase of hydrogen permeation current at first potential drop,

and then the current increase with increasing the rest potential. During the drying, the current remains large values while the potential increases. The low correlation between the potential and the hydrogen permeation current is due to the low diffusion constant of the steel. The hybrid technique of Laser and micro-cell to apply investigate hydrogen preferentially intrusion site was carried out. The observed diffusion constant by the technique showed same order as reported one. The results indicated that grain boundary may be the preferentially site for hydrogen intrusion.

(4) Effect of metal cations on corrosion behavior of aluminum alloys in model tap water

It has been reported that the corrosion rate of aluminum alloy in model tap water is affected by kind of metal cation in the media, and the effect can be explained by metal cation hardness which based on the hard and soft acid and base, HSAB, concept. The effect of kind of metal cations on the galvanic corrosion behavior of A3003 aluminum alloy in model tap waters was examined by electrochemical noise impedance. The electrochemical noise impedance and conductance were calculated by the power spectrum density, that calculated with FFT, of the galvanic current and potential. The sum of the galvanic current during galvanic corrosion tests was suppressed by the addition of  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ , while it was increased with  $\text{Mg}^{2+}$  addition. These results may be explained by the passive film structure changes due to the metal cations. The surface oxide films of aluminum alloys after immersed in the model tap waters were observed by XPS.

(5) The effect of  $\text{CH}_3\text{COONa}$  concentration on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments

An acetic acid is the most common organic acid in oil and gas environments, therefore, acetate ions sometimes used in simulated oil and gas environments. However, the role of acetic ions in corrosion behavior and surface film structure. In this year, the surface film structure change with immersion period especially sort immersion time was investigated by XPS. Addition of  $\text{CH}_3\text{COONa}$  and longer immersion time lead to small hole formation and surface color change. Even in high concentration of  $\text{CH}_3\text{COONa}$  and high temperature, surface film thickness less than 5 nm. The film thickness, however, is affected by immersion condition.

(6) Formation of hydrophobic porous alumina films on aluminum alloy by desiccation treatment and the corrosion resistance



Diminishing surface wettability is an effective method to improve corrosion resistance of aluminum. The novel technique to increasing wettability by anodizing and desiccation is applied to A1050 aluminum alloy. The water contact angle of anodized samples increases considerably with desiccation treatment. The maximum water contact angle of 140 degree was achieved by the treatment. However, there was no considerable effect of polishing and anodizing time. There is an increase in the corrosion resistance of the samples in 3.5 mass% NaCl solution with an increase in the water contact angle, and also anodized and desiccated samples showed a better corrosion resistance than un-desiccated samples.

#### 7) Formation of composite oxide films for dielectric materials by anodizing and LPD

As NaOH used to control pH of the Liquid Phase Deposition treatment (LPD), LPD and anodizing process can form  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite layer and it shows very high capacitance. However, NaF layer also deposited on the substrate, and this layer was expected to reduce the phase shift. Therefore, NaOH and KOH mixed solution was used. It is possible to form  $\text{TiO}_2$  layer by this solution, however, it is difficult to avoid NaF deposition.

#### 8) Multi layer structured of Cu-Ni with nano-size thickness film formation and its property

DC electro-deposition Cu-Ni nano thickness multi layer formation machine was developed. Using Ti as substrate, makes it possible to peel off the formed Cu-Ni film easily. The layer structure was observed by FIB-SEM.

#### 9) Field exposer test in cold and heavy snow district

The filed exposer test for corrosion of steels in cold and heavy snow district as Sapporo and Akkeshi in Hokkaido have been started. This exposer test is a joint research work of e-Asia corrosion mapping project, NIMS. From carried out the test, it must be take care piled up snow level

#### Other activities

In July Assoc. Prof. Sakairi attended 9th International Symposium on Electrochemical Impedance Spectroscopy, EIS2014 at Okinawa, Japan and presented a paper entitled "Evaluation of Effect of Metal Cations on Galvanic Corrosion Behavior of Al alloy by Impedance". He also attended attended

HU-AGH symposium at Sapporo, Japan and presented a paper entitled "Local surface modification by solution flow type micro-droplet cell".

In August, Dr. Ningshen attended The Stainless Steels Centenary Symposium SSCS 2013 at Mumbai, India and presented paper entitled "Corrosion resistance of 9-15% Cr ODS steels and its Comparison with Austenitic Stainless Steels".

In August, Assoc. Prof. Sakairi attended 16th International Conference on Environmental Degradation of Materials in Nuclear Power system- Water Reactors ad Asheville, USA and presented the paper entitled "Oxide Films on Nickel-base Alloys in Water at 360 °C under PWR Environment.

In September, Assoc. Prof. Sakairi attended EUROCORR2013 at Estoril, Portugal presented a paper entitled "Effect of the metal cations in model tap water on corrosion behaviour and passive film structure of Al".

In October, Assoc. Prof. Sakairi attended 5th International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems, LongTermCorr 2013 at Asahikawa, Japan.

In November Assoc. Prof. Sakairi attended NACE international East Asia & Pacific Rim Area conference & Expo 2013 at Kyoto, Japan and presented a paper entitled "Effect of sodium acetate in model oil and gas environments on oxide film structure and corrosion behavior of 13%Cr stainless steel".

## Presentations

Effect of substrate composition on efficiency of hydrogen entry, S. Takagi and M. Sakairi, The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, Jan., 2013.

Anodic film formation at elected area by Sf-MDC -Effect of electrode shape-, T. Yamaguchi, M. Sakairi and K. Fushimi, *ibid*.

Corrosion behavior of 13%Cr stainless steel in acid 5 mass% NaCl, M. Matsutomo, M. Sakairi, T. Tanigushi and S. Hasizume, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, Jan., 2013.

Formation of high dielectric oxide layer on Al by LPD and anodizing, T. Sasaki, M. Sakairi, S. Nagata, *ibid*.

Formation of nano-porous Al oxide layer on Al-Zn lining in Phosphoric acid, M. Ishida, T. Ohmi, M. Sakairi and K. Iwai, *ibid.*

Polarization behavior of A3003 in model tap water with different metal cations, R. Sasaki, M. Sakairi and A. Kaneko, *ibid.*

Anodizing of Al-Zn micro-channel inner wall in phosphoric acid, M. Ishida, T. Ohmi, M. Sakairi and K. Iwai, Spring meeting of ISIJ, Tokyo, March, 2013.

Effect of metal cations on Al oxide film composition, M. Sakairi, K. Otani, R. Sasaki and A. Kaneko, Spring meeting of Jpn. Inst. Metals, Tokyo, March 2013.

M. Sakairi, Y. Yang and M. Zheng, Wettability and corrosion resistance change of porous type Al anodic oxide film with desiccation process, The 80th meeting of Electrochemistry Japan, Sendai, March 2013.

Oxide film structure and composition of Ni alloy formed in PWR environment, T. Ohtsuka, Y. Hamaguchi, M. Sakairi, K. Fushimi, Y. Sakakibara, G. Nakayama, Zairyo-to-Kankyo 2013, May, Tokyo, 2013.

Analysis of oxide film formed on Al alloys in model tap water, R. Sasaki, M. Sakairi, A. Kaneko, Y. Seki and D. Nagasawa, *ibid.*

Changes of oxide film composition of Al alloys formed in model tap waters, M. Sakairi, R. Sasaki and A. Kaneko, The 73th discussion meeting of J. Anal. Soc., Hakodate, 2013.

M. Sakairi, T. Yamaguchi and T. Murata, Local surface modification by solution flow type micro-droplet cell, HU-AGH symposium, Sapporo, June, 2013.

Evaluation of Effect of Metal Cations on Galvanic Corrosion Behavior of Al alloy by Impedance, M. Sakairi, A. Kaneko, R. Sasaki, Y. Seki and D. Nagasawa, EIS2013, Okinawa, June, 2013.

Effect of coating of Sf-MDC Pt electrode on formed alumina size, T. Yamaguchi, M. Sakairi and K. Fushimi, The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Muroran, July, 2013.

Chemical composition of oxide film formed on Al in  $\text{SO}_4^{2-}$  solutions by XPS, R. Sasaki, M. Sakairi and A. Kaneko, *ibid.*

Oxide Films on Nickel-base Alloys in Water at 360 °C under PWR Environment has been accepted into the PWR Primary SCC, T. Ohtsuka, Y. Hamaguchi, M.

Sakairi, K. Fushimi, K. Azumi, Y. Sakakibara, and G. Nakayama, 6th International Conference on Environmental Degradation of Materials in Nuclear Power system-Water Reactors at Asheville Asheville, USA, August, 2013.

Corrosion resistance of 9-15% Cr ODS steels and its Comparison with Austenitic Stainless Steels, S. Ningshen, M. Sakairi, K. Suzuki and S. Ukai, The Stainless Steels Centenary Symposium SSCS 2013, Mumbai, India, August, 2013

Effect of metal cations in model tap water on corrosion behaviour and passive film structure of Al, M. Sakairi, M. Sakairi, K. Otani, R. Sasaki, A. Kaneko, Y. Seki and D. Nagasawa, Eurocorro 2013, Estoril, Portugal, September, 2013.

Analysis of iron Passive structure by XPS and AES, M. Sakairi, M. Abe, S. Ningshen and T. Ohtsuka, Autumn meeting of ISIJ, Kanazawa, September, 2013.

Wettability change with drying process of porous type anodic oxide film formed on aluminum alloy and its effect on corrosion resistance, M. Sakairi, G. Varitant, M. Zheng, Autumn meeting of Electrochemical Soc. Jpn., Tokyo, September, 2013.

Area selective porous type anodic aluminum oxide film formation by Sf-MDC-Effect of coating on film growth behavior-, T. Yamaguchi, M. Sakairi, K. Fushimi, The 128th meeting of Surf. Fin. Soc. JPN, Fukuoka, September, 2013.

Structure change of passive film formed on Al alloy with temperature and immersion time in model tap waters, R. Sasaki, M. Sakairi, A. Kaneko, Y. Seki and D. Nagasawa, The 60th Discussion meeting of Ziryo-to-Kankyo, Fkushima, September, 2013.

Effect of temperature on passive film structure formed on Al alloys in dilute solution, R. Sasaki, M. Sakairi, Corrosion dream 2013, Sapporo, October, 2013.

Area selective anodizing by Sf-MDC, M. Sakairi, T. Yamaguchi and T. Murata, The 40th ARS conference, Hirosaki, November, 2013.

Effect of sodium acetate in model oil and gas environments on oxide film structure and corrosion behavior of 13%Cr stainless steel, M. Sakairi, A.Kikawa, S. Hashizume, T. Taniguchi, NACE international East Asia & Pacific Rim Area conference & Expo 2013, Kyoto, Japan, November, 2013.

## AFFILIATE MEMBER

Assoc. Prof. Dr. Shigenari Hayashi  
Tel.:+81-11-706-6357 Fax.:+81-11-706-7814  
E-mail:hayashi@eng.hokudai.ac.jp

Presently  
Department of Metallurgy and Ceramics Science  
Graduate School of Science and Engineering  
Tokyo Institute of Technology  
Tel&Fax: +81-3-5734-3585  
E-mail:s.hayashi@mtl.titech.ac.jp

## Students

S. Najima, K. Kaya, F. Tsutsumi, S. Yoneda, T. Kudo, D. Takashima, T. Miura,  
and Y. Shizukawa

The research activities of the laboratory are directed to the high-temperature oxidation and corrosion of alloys and coatings. Our particular interests are an understanding of the mechanism of the high temperature oxidation of metals such as superalloys, intermetallic compounds, Fe or Ni-based heat resistant alloys, and steels.

Current topics on research are in the following:

(1) Effect of Cr on the development of  $\text{Al}_2\text{O}_3$  scale on Fe and/or Ni based alloys

Cr addition is known to decrease the critical Al content to form an external  $\text{Al}_2\text{O}_3$  scale on both Fe- and Ni-based alloys and coatings. This beneficial Cr effect is speculated that Cr decreases oxygen inward diffusion due to formation of a protective  $\text{Cr}_2\text{O}_3$  scale at initial stage of oxidation, promoting exclusive  $\text{Al}_2\text{O}_3$  scale formation. In order to verify this speculation of Cr effect, development of oxide scale during an initial transient stage of oxidation on Cr-coating Ni- or Fe-based alloys is being investigated systematically by in-situ high-temperature X-ray diffraction analysis by means of synchrotron radiation.

## (2) High Temperature oxidation of Cu-modified austenitic Fe-Ni-Cr-Al alloys

Higher Al content is required to form external  $\text{Al}_2\text{O}_3$  scale on austenitic heat resistant alloy substrate. Therefore high-Al intermetallic phases such as  $\beta\text{-NiAl}$ ,  $\gamma'\text{-Ni}_3\text{Al}$  and  $\alpha\text{-Cr}$  often formed in  $\text{Al}_2\text{O}_3$  forming austenitic alloys. Formation of those intermetallic phases makes the alloy manufacturing by such as a hot-rolling difficult. Therefore development of new  $\text{Al}_2\text{O}_3$  scale forming austenitic heat resistant alloys with low-Al content is strongly requested. We recently found that Cu decreases critical Al content for formation of an  $\text{Al}_2\text{O}_3$  scale on austenitic Fe-Ni-Cr-Al alloys. The reason(s) of this beneficial effect of Cu on  $\text{Al}_2\text{O}_3$  scale formation is now being explored.

## (3) Oxidation of austenitic Fe-Ni-Cr alloys in water vapor

Austenitic heat resistant stainless steels are widely used as materials for boiler tubes. The oxidation resistance of stainless steels in high-temperature water vapor is known to depend on alloy Ni content. In this study the effect of Ni on oxidation behavior of Fe-Ni-Cr alloys is being investigated. Oxidation mass gain decreased with increased Ni content but it increased rapidly on a binary Ni-Cr binary alloy. The dependence of Ni content on the oxidation behavior in air and water vapor was similar, but oxidation mass gain in water vapor was much greater than that in air.

## (4) Oxidation and carburization behavior of Fe-low Cr alloys

Fe-low Cr steels are widely used as boiler tube materials of fossil fuel combustion power generation plants. In order to decrease  $\text{CO}_2$  emission from fossil fuel power plants,  $\text{CO}_2$  capturing technique with oxyfuel combustion is being proposed. Under the oxyfuel combustion, materials in a boiler are exposed in atmospheres with higher  $\text{CO}_2$  content. Therefore evaluation of oxidation behavior of Fe-low Cr alloys in  $\text{CO}_2$  is necessary. In this study, we found that the excess oxygen in  $\text{CO}_2$  containing atmosphere decreases the oxidation mass gain by preventing the internal carburization, which causes breakaway of protective  $\text{Cr}_2\text{O}_3$  scale. This result suggests that initially formed  $\text{Cr}_2\text{O}_3$  scale contains defects such as hair-cracks, which allow penetration of  $\text{CO}_2$  gas molecules across the  $\text{Cr}_2\text{O}_3$  scale, and those defects may be healed by excess oxygen. We also found that a thin amorphous  $\text{SiO}_2$  layer formed below a  $\text{Cr}_2\text{O}_3$  scale prevents carbon penetration into the alloy substrate.

## Presentations

Phase transformation behavior of  $\text{Al}_2\text{O}_3$  scale formed on Fe-Ni-Al alloys; Y. Takada, S. Hayashi, and S. Ukai: JSPS 123 committee research workshop, May, 2013.

Effect of alloying elements on the internal oxidation kinetics of Fe-Si-X alloys; F. Tsutsumi, S. Hayashi, M. Maruyama, S. Ukai: The Spring Meeting of Jpn. Inst. Metals, Tokyo, Japan, May, 2013.

Phase transformation behavior of FeO scale in low partial pressure of oxygen; S. Yoneda, S. Hayashi, H. Tanei, Y. Kondo, and S. Ukai: The Spring Meeting of Jpn. Inst. Metals, Tokyo, Japan, May, 2013.

Effect of Fe on the phase transformation of  $\text{Al}_2\text{O}_3$  formed on  $\beta$ -Ni-Fe-Al alloys; S. Hayashi, Y. Takada, and S. Ukai: The Spring Meeting of Jpn. Inst. Metals, Tokyo, Japan, May, 2013.

Role of Fe for the metastable to stable phase transformation of  $\text{Al}_2\text{O}_3$  scale; S. Hayashi, Y. Takada, S. Ukai: Gordon research conference, high-temperature oxidation, NH, USA, 2013.

Mechanism of isothermal phase transformation of FeO scale; S. Yoneda, S. Hayashi, H. Tanei, Y. Kondo, and S. Ukai: Gordon research conference, high-temperature oxidation, NH, USA, 2013.

High-temperature oxidation behavior of Fe-9Cr steel in  $\text{CO}_2$ - $\text{O}_2$  gas mixture ; K. Kaya, S. Hayashi, and S. Ukai: Adv. In Mater. Tech. for Fossil Power Plants, Hawaii, USA, Oct. 2013.

Effect of Cr on the formation of  $\text{Al}_2\text{O}_3$  scale on Ni-Al-Cr alloys : The Autumn Meeting of Jpn. Inst. Metals, Kanazawa, Japan, Sep., 2013.

Effect of Ni and Al on oxidation of Fe-Cr-Ni-Al; D. Kudo, S. Hayashi, and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Kanazawa, Japan, Sep., 2013.

Effect of Ti or Al on internal oxidation of Fe-Si alloys; F. Tsutsumi, S. Hayashi, M. Maruyama, and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Kanazawa, Japan, Sep., 2013.

Effect oxygen on high-temperature oxidation of Fe-9Cr steel in  $\text{CO}_2$ - $\text{O}_2$  mixture ; K. Kaya, S. Hayashi, and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals,

Kanazawa, Japan, Sep., 2013.

Effect of Ni on oxidation of austenitic Fe-Cr-Ni stainless steel; D. Takashima, S. Hayashi, Y. Nishiyama, and S. Ukai: The Autumn Meeting of Jpn. Inst. Metals, Kanazawa, Japan, Sep., 2013.

The effect of Cr on the critical Al content for  $Al_2O_3$  scale formation; S. Yoneda, S. Hayashi, and S. Ukai: JSPS 123 committee research workshop, Nov., 2013.

Influence of gas composition fluctuation on sulfidation behavior of low alloy steel in simulated coal combustion atmosphere; S. Najima, S. Hayashi, and S. Ukai: JSPS 123 committee research workshop, Nov., 2013.



**ABSTRACT of PUBLICATIONS**



## **Electrochemical synthesis of polypyrrole films on copper from phytic solution for corrosion protection**

Y. Lei, N. Sheng, A. Hyono, M. Ueda, T. Ohtsuka

*Corrosion Science*, **76**, 302-309 (2013)

Phytic acid ( $C_6H_{18}O_{24}P_6$ ), the principal phosphorous storage form in many plant tissues, is a green material. A polypyrrole (PPy) doped with phytic acid ( $IP_6$ ) was electrosynthesised on copper from an aqueous phytic acid solution. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and SEM were used to characterise the polymer. The polymer-covered copper was subjected to a corrosion test in NaCl solution. The dissolution of copper covered with PPy- $IP_6$  was found to be greatly inhibited in NaCl solution. The inhibition indicated protection of the PPy- $IP_6$  layer against copper corrosion.

## **Visualizing Preparation Using Asymmetrical Choline-Like Ionic Liquids for Scanning Electron Microscope Observation of Non-Conductive Biological Samples**

S. Abe, A. Hyono, K. Kawai, T. Yonezawa

*Journal of Nanoscience and Nanotechnology*, **13**, 1-4 (2013)

In this study, we investigated conductivity preparation for scanning electron microscope (SEM) observation that used novel asymmetrical choline-type room temperature ionic liquids (RTIL). By immersion in only an RTIL solution, clear SEM images of several types of biological samples were successfully observed. In addition, we could visualize protozoans using RTILs without any dilution. These results suggested that the asymmetrical choline-type RTILs used in this study are suitable for visualizing of biological samples by SEM. Treatment without the need for dilution can obviate the need for adjusting the RTIL concentration and provide for a rapid and easy conductivity treatment for insulating samples.

## **Scanning Electron Microscope observation of nano carbon materials with imidazolium-type room temperature ionic liquids**

S. Abe, A. Hyono, K. Nakayama, T. Takada and T. Yonezawa

Japanese Journal of Applied Physics, **52**, 01AH02

A novel pre-treatment method for scanning electron microscopy (SEM) observation using room temperature ionic liquids (ILs) was used for several carbon nano materials. After the ILs pre-treatment, the quality of the SEM images obtained was almost the same as that obtained with conventional platinum/palladium (Pt/Pd) sputtering pre-treatment. The highest resolution in this study was under 30 nm. This result means that the pre-treatment with IL can form ultrathin layer on the sample surface at several molecules level. Therefore, the ILs pre-treatment is a simple and easy tool for SEM observation of nano materials on insulating substrates.

## **Pure-Shear Test for Investigation of Non-Basal Slip System Operation of Mg Alloy Single Crystal with and without Y**

Takahiro Mineta, Seiji Miura, Toshiji Mukai, Mikito Ueda, Tetsuo Mohri

Journal of the Japan Institute of Metals and Materials, **77** (2013) 466-472

In Mg alloys, the most favorable deformation mechanism is the basal slip, and extension twinning also contributes to plastic deformation. Other mechanisms such as prismatic slips, pyramidal slips and twinning except for extension twinning scarcely occur. However, these slip systems also contribute to the plastic deformation of poly crystal Mg alloys, so the determination of CRSS of such non-basal slip systems are inevitable as a basis for the prediction of the deformation behavior of poly-crystal Mg alloys. Because of the difficulty of the evaluation of CRSS for non-basal slip by conventional compression test, newly designed "Pure shear test" is applied to evaluate the CRSS of the prismatic slip Mg alloy single crystals containing Y. Also a modification of Bridgman method using LiF+LiCl is attempted to obtain a pure-Mg single crystal.

## **Electrorefining reaction of sodium in sodium-bis(trifluoromethylsulfonyl) imide and tetraethylammonium-bis(trifluoromethylsulfonyl) imide mixture ionic liquid**

Mikito Ueda, Kazuya Honda, Toshiaki Ohtsuka

*Electrochimica Acta*, **100** (2013) 265–268

To develop a electrorefining process of sodium for the recycling of used sodium–sulfur secondary battery, a non-aqueous electrolytic melt was investigated as a candidate for the process. A mixed ionic liquid of NaTFSI (sodium-bis(trifluoromethylsulfonyl)imide)–TEATFSI (tetraethylammonium-bis(trifluoromethylsulfonyl)imide) was selected for the electrolyte, since it has a wide potential window and a weak reactivity with metallic sodium. From AC impedance measurements, the maximum electric conductivity of  $36 \text{ mS cm}^{-1}$  was found for a concentration of 20 mol% NaTFSI–TEATFSI at 433 K. The cathodic deposition of liquid sodium, 99.99% pure, was obtained on a glassy carbon electrode by constant current electrolysis. The calcium concentration in the sodium was decreased from 500 to 12 ppm by the electrorefining. A cathodic current efficiency at 88% was achieved in these electrorefining experiments.

## **Composition and structure of Al–Sn alloys formed by constant potential electrolysis in an $\text{AlCl}_3\text{–NaCl–KCl–SnCl}_2$ molten salt**

Mikito Ueda, Ryuich Inaba, Toshiaki Ohtsuka

*Electrochimica Acta*, **100** (2013) 281–284

To form Al–Sn alloys for bearing materials, molten salt electrolysis was performed in an  $\text{AlCl}_3\text{–NaCl–KCl}$  molten salt containing  $\text{SnCl}_2$  at 423 K. The voltammogram showed that the cathodic reduction of the Sn ions started at a potential of 0.5 V vs. Al/Al(III) in the molten salt showing that deposition of pure Sn was possible at 0.5 V. Co-deposition of Al and Sn occurred at potentials more negative than 0.1 V. The co-deposit was composed a solid solution of Al and Sn. The ratio of the Sn in the electrodeposits decreased with the potential from 100 at.% at 0.2 V to 19 at.% at  $-0.3$  V. In the structural observations, electrodeposits with an alternate stacked structure of Al and Sn is obtained at  $-0.075$  V.

## **The formation of polypyrrole film on zinc-coated AZ91D alloy under constant current characterized by Raman spectroscopy**

Nan Sheng, Mikito Ueda, Toshiaki Ohtsuka

*Progress in Organic Coatings*, **76** (2013) 328–334

The electropolymerization of conducting polypyrrole (PPy) film on zinc-coated AZ91D magnesium alloy under constant current control in aqueous sodium tartrate containing pyrrole monomer was investigated using Raman spectroscopy and surface observation. Zinc oxide and zinc hydroxide are initially formed, which are then replaced by a zinc tartrate salt layer. The PPy nucleation is initiated on the zinc layer covered by zinc tartrate, followed by three-dimensional growth of the PPy layer.

## **Output properties of an Al-Cl<sub>2</sub> cell in AlCl<sub>3</sub>-EMIC ionic liquid**

Mikito Ueda, Hajime Matsunaga, Toshiaki Ohtsuka

*Electrochimica Acta*, **100** (2013) 281–284

To develop an aluminum-chlorine cell, an electrochemical cell consisting of an aluminum anode and a graphite cathode was developed and evaluated in EMIC- AlCl<sub>3</sub> ionic liquid.

The open circuit voltage of the aluminum-chlorine cell was about 1.8-1.9 V after introduction of chlorine gas to 66.7 mol% EMIC-AlCl<sub>3</sub> at 303 K. The relationship between current density and cell voltage in the cell showed an almost linear relation. The major factor in the voltage drop of the output voltage was considered to be due to resistance of electrolytic melt. The output characteristics of the cell depend on the configuration of the graphite cathode, the current density with a step type cathode at 0.5 V was about 20 % better than that of a cylindrical type graphite cathode.

## **Hydrogen Membrane Fuel Cells with Metal/Insulator/Metal Structure**

Y. Aoki, R. Nonaka and H. Habazaki

*ECS Transactions*, **57**, 911-916 (2013)

Novel thin film fuel cell based on the 100 nm-thick electrolyte of amorphous ZrP<sub>2.5</sub>O<sub>x</sub>, working at 400°C, was demonstrated. The hydrogen permeable membrane fuel cell (HMFC) using a Pd foil as a nonporous solid anode was fabricated. Ni interlayer of several hundreds nm thickness was introduced between the Pd anode and the ZrP<sub>2.5</sub>O<sub>x</sub> electrolyte in order to suppress the deterioration of the electrolyte nanofilm by the deformation of the Pd anode during hydrogen absorption. In the ZrP<sub>2.5</sub>O<sub>x</sub> electrolyte the transport number of proton was unity at 400°C as determined by an EMF measurement. The modification of the Ni anode surface by an ultrathin Pt or Pd layer effectively decreased the anode/electrolyte interfacial polarization. Consequently, the HMFC revealed the OCV of 1.0 V and the maximum power density of 3.6 mW cm<sup>-2</sup> at 400°C.

## Tracer Study of Pore Initiation in Anodic Alumina Formed in Phosphoric Acid

A. Baron-Wiecheć, M.G. Burke, T. Hashimoto, H. Liu, P. Skeldon, G.E. Thompson, H. Habazaki,

J.J. Ganem and I.C. Vickridge

*Electrochimica Acta*, **113**, 302-312 (2013)

Arsenic species are utilized as tracers in a study of pore initiation in anodic films that were formed at constant potentials on aluminium in phosphoric acid. The films were grown first in sodium arsenate solution and then in phosphoric acid, and examined using ion beam analysis and scanning and transmission electron microscopies. The analysis of the arsenic content of specimens indicates that the growth mechanisms of incipient and major pores involve mainly field-assisted dissolution and field-assisted flow of the alumina, respectively. The transition between incipient and major pore formation is suggested to be initiated by preferential growth of certain incipient pores, leading to a locally increased current density at the pore bases. The major pores subsequently develop by the flow oxide away from the pore bases, which is evident from the behaviour of the arsenic tracer. The results suggest that the flow is associated with the non-uniform distribution of ionic current and a relatively low volume of formed film material compared with the volume of oxidized aluminium.



## **Photoelectrochemical Characterization of Amorphous Anodic Films on Ti–6at.%Si**

F. Di Quarto, F. Di Franco, C. Monarca, M. Santamaria and H. Habazaki

*Electrochimica Acta*, (2013)

The solid state properties of anodic films grown galvanostatically on sputtering-deposited Ti–6at.%Si alloys were studied as a function of the formation voltage (5–40 V). From the photocurrent spectra a band gap of  $\sim 3.4$  eV was estimated for all the investigated thicknesses, which is almost coincident with the value measured for amorphous TiO<sub>2</sub>. The photocharacteristics allowed to estimate the flat band potential of the films, which resulted to be more anodic for thicker layers and allowed to evidence a change from n-type semiconducting material to insulator by increasing the formation voltage. A dielectric constant of  $\sim 31$  was estimated by differential capacitance measurements. The dependence of photocurrent on electrode potential was studied in the frame of Onsager–Braun theory, which allows to evidence the influence of the initial recombination on the photocurrent yield for amorphous material.

## **Fabrication of Super-oil-repellent Surfaces by Two-step Anodizing of Aluminum**

H. Habazaki, T. Fujii, E. Tsuji and Y. Aoki

*ECS Transactions*, **50**, 217-224 (2013)

In this study, hierarchical dual pore surfaces have been developed by two-step anodizing of aluminum. The first anodizing has been carried out at 390 V in 2 wt% citric acid, and then, the resultant anodic film has been dissolved to disclose the scalloped aluminum substrate with a cell size of  $\sim 900$  nm. Subsequently, the second anodizing has been carried out at 25 V in 0.3 mol dm<sup>-3</sup> sulfuric acid electrolyte to generate smaller nanopores. The size of nanopores has been further controlled by pore-widening treatment in 5 wt% phosphoric acid at 303 K. After coating with a fluoroalkyl phosphate monolayer to reduce the surface energy, the dual pillar surfaces with enlarged nanopores show super-repellency even for rapeseed oil as well as for water.

## The Effects of Film Thickness and Incorporated Anions on Pitting Corrosion of Aluminum with Barrier-type Oxide Films Formed in Neutral Borate and Phosphate Electrolytes

H. Habazaki, R. Nishimura, K. Okitsu, H. Inoue, I. Kiriya, F. Kataoka, M. Sakairi and H. Takahashi

Journal of Solid State Electrochemistry, (2013)

The pitting corrosion behavior of high-purity aluminum covered with barrier-type anodic films, which are formed in neutral borate and phosphate electrolytes, has been examined in  $0.5 \text{ mol dm}^{-3}$  NaCl solution at an applied potential of  $-0.6 \text{ V}$  versus Ag/AgCl, which is slightly nobler than the pitting potential of  $-0.64 \text{ V}$  in the same solution. The pitting current density,  $i_p$ , increased with time after an incubation time,  $t_i$ . The double logarithmic plot of  $i_p$  and polarization time,  $t$ , reveal two straight lines, which are separated at the time,  $\tau$ . The slope becomes larger after  $\tau$  for the specimens anodized in the phosphate electrolyte, while it becomes smaller for those in the borate electrolyte. Both the  $t_i$  and  $\tau$  increase with the thickness of the anodic films, and at the similar film thickness, they are much larger for the anodic films formed in the phosphate electrolyte than for those in the borate electrolyte. The corrosion process can be divided into three stages: the incubation period up to  $t_i$ , the pit nucleation period before  $\tau$ , and the pit growth period after  $\tau$ . We have discussed the different pitting corrosion behavior of the aluminum specimens covered with the anodic films formed in the borate and phosphate electrolytes in terms of ion selectivity of the anodic films.

## **The Use of Renewable Energy in The Form of Methane via Electrolytic Hydrogen Generation**

K. Hashimoto, N. Kumagai, K. Izumiya, H. Takano, P.R. Zabinski, A.A. El-Moneim, M. Yamasaki, Z. Kato, E. Akiyama and H. Habazaki

Archives of Metallurgy and Materials, **58**, 231-239 (2013)

Extrapolation of world energy consumption from 1990 to 2010 indicates the complete exhaustion of world reserves of oil, natural gas, uranium and coal by 2040, 2043, 2046 and 2053, respectively. For the survival of all people in the whole world, intermittent and fluctuating electricity generated from renewable energy should be supplied in the form of usable fuel to all people in the whole world. We have been working on research and development of global carbon dioxide recycling for the use of renewable energy in the form of methane via electrolytic hydrogen generation using carbon dioxide as the feedstock. We created energy-saving cathodes for hydrogen production, anodes for oxygen evolution without chlorine formation in seawater electrolysis, and catalysts for methanation of carbon dioxide and built pilot plants of industrial scale. Recent advances in materials are described. Industrial applications are in progress.

## **Formation and Dielectric Properties of Anodic Films Formed on Ta-W Alloys at Various Formation Voltages**

M. Ishizuka, E. Tsuji, Y. Aoki and H. Habazaki

Electrochemistry, **81**, 840-844 (2013)

Barrier-type anodic films are formed on magnetron sputtered Ta-W alloy films to various formation potentials in  $0.1 \text{ mol dm}^{-3}$  ammonium pentaborate electrolyte. The anodic films consist of two layers, comprising an outer thin  $\text{Ta}_2\text{O}_5$  layer free from tungsten species and an inner layer containing both tantalum and tungsten species. Slower migration of  $\text{W}^{6+}$  ions with respect to  $\text{Ta}^{5+}$  ions results in the formation of the two-layered films. Because of the absence of more soluble tungsten species in the outer layer, the anodic films grow at high current efficiency. The reciprocal of capacitance of the anodic films changes linearly with formation voltage, as a consequence of linear thickening of the anodic films with the formation potential. The capacitance is enhanced by the addition of tungsten, particularly at low formation potential. The shift of the potential, at which the anodic film growth commences, to the noble direction, contributes to the enhanced capacitance at the low formation voltages.

## **Influence of Yttrium Addition on the High Capacitance of $ZrO_2$ - $SiO_2$ Nanocomposite Anodic Oxide Films**

M. Ishizuka, E. Tsuji, Y. Aoki, A. Hyono, T. Ohtsuka, N. Sakaguchi, S. Nagata and H. Habazaki

ECS Transactions, **50**, 245-254 (2013)

The sputter-deposited Zr-Si-Y film was anodized to form a high capacitance composite anodic film, comprising a tetragonal  $ZrO_2$  nanocrystalline phase and a silicon-enriched amorphous phase. It was found that the nanocomposite anodic film, as well as the yttrium-free  $ZrO_2$ - $SiO_2$  anodic film, showed markedly increased capacitance compared with the anodic film  $ZrO_2$  film on zirconium. The incorporation of yttrium species to the anodic  $ZrO_2$ - $SiO_2$  film did not change the thickness and permittivity of the anodic oxide film, although a thicker anodic film was formed on zirconium by the incorporation of yttrium, which may introduce oxygen vacancies in the crystalline  $ZrO_2$ . The findings suggest that in the composite  $ZrO_2$ - $SiO_2$  anodic films the film thickness is mainly controlled by the silicon-enriched amorphous phase.

## **Formation of Self-organized Nanoporous Anodic Films on Carbon Steel**

Y. Konno, S. Yang, E. Tsuji, Y. Aoki, P. Skeldon, G.E. Thompson and H. Habazaki

ECS Transactions, **50**, 183-190 (2013)

The growth behavior of nanoporous anodic films on carbon steel containing 0.213 mass% carbon has been examined during anodizing in ethylene glycol containing  $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{F}$  and  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{O}$ . The nanopores in the anodic films are generated preferentially along with steps and at “kink-like” sites of the steel surface generated by rf-GD sputtering. The steel contains carbide precipitates with a size of 50-800 nm. The anodic oxide formed on the carbide phase is more chemically soluble during anodizing, producing pits in the anodic films.

## **Physicochemical Characterization and Photoelectrochemical Analysis of Iron Oxide Films**

M. Santamaria, S. Terracina, Y. Konno, H. Habazaki and F. Di Quarto

Journal of Solid State Electrochemistry, **17**, 3005-3014 (2013)

Iron oxide films with a nanoporous structure were grown by anodizing sputter-deposited Fe in a fluoride containing ethylene glycol solution and annealed under air exposure at different temperatures. X-ray diffraction and Raman spectroscopy allowed to identify the presence of hematite and/or magnetite after thermal treatment for films annealed at  $T \geq 400$  °C under air exposure. According to GDOES compositional depth profiles, the thermal treatment sensitively reduced the amount of fluoride species incorporated into the film during the anodizing process. A band gap value of  $\sim 2.0$  eV was estimated for all the investigated layers, while a flat band potential dependent on both the growth conditions as well as on the annealing temperature was estimated.

## **Observation of self-assembled layers of alkyl phosphonic acid on aluminum using low-voltage scanning electron microscopy and AFM**

H. Sato, T. Fujii, E. Tsuji, Y. Aoki, K. Shimizu, P. Skeldon, G.E. Thompson and H. Habazaki

Surface and Interface Analysis, **45**, 1441-1445 (2013)

Self-assembled alkyl phosphate layers have been formed on a flat, anodized aluminum substrate in dilute ethanol solution containing 2wt% n-tetradecylphosphonic acid (TDP) and examined by low-voltage scanning electron microscopy as well as atomic force microscopy and X-ray photoelectron spectroscopy. Locally, multi-layered alkyl phosphate films have been formed on aluminum, being clearly observed by a low-voltage scanning electron microscope operated at less than 1 kV. Atomic force microscopy observations disclosed that bilayers of tetradecylphosphonic acid are stacked on the substrate to form multilayers. The present study revealed that the uniform self-organized monolayer is not always formed readily on an oxidized aluminum surface.

## **Preparation of Non-Annealed Anatase TiO<sub>2</sub> Film on ITO Substrate by Anodizing in Hot Phosphate/Glycerol Electrolyte for Dye-Sensitized Solar Cells**

E. Tsuji, N. Hirata, Y. Aoki and H. Habazaki

Materials Letters, **91**, 39-41 (2013)

In this study, mesoporous TiO<sub>2</sub> films were formed on ITO conductive glasses by anodizing of titanium thin films without post-annealing. The titanium thin films, ~ 200 nm thick, sputter-deposited on to the ITO substrates were anodized at 20 V in a phosphate/glycerol electrolyte at 433 K. A completely transparent TiO<sub>2</sub> specimen was obtained by anodizing for 60 s. The as-anodized mesoporous TiO<sub>2</sub> films consisted of anatase, even without post-annealing. The transparent mesoporous TiO<sub>2</sub> films anodized for a suitable time showed much better photoelectrochemical performance than the post-annealed TiO<sub>2</sub> nanotubular film.

## Compositional Dependence of the Proton Conductivity of Anodic ZrO<sub>2</sub>-WO<sub>3</sub>-SiO<sub>2</sub> Nanofilms at Intermediate Temperatures

K. Ye, Y. Aoki, E. Tsuji, S. Nagata and H. Habazaki

Journal of the Electrochemical Society, **160**, F1096-F1102 (2013)

Novel proton-conducting ZrO<sub>2</sub>-WO<sub>3</sub>-SiO<sub>2</sub> nanofilms of various compositions and thicknesses (~ 50 to ~ 300 nm) have been prepared by anodizing of magnetron-sputtered Zr-W-Si alloys in 0.1 mol dm<sup>-3</sup> phosphoric acid electrolyte at 20°C. All the anodic oxide nanofilms examined reveal efficient proton conductivity after post-annealing at 250°C. Further increase in the post-annealing temperature results in the conductivity degradation for the anodic oxide nanofilms on the alloy containing only 5 at% silicon, while the high conductivity is maintained even after post-annealing at 300°C for those containing 15 at% or more silicon. The proton conductivity is dependent upon tungsten content; the conductivity of  $5 \times 10^{-6}$  S cm<sup>-1</sup> for the ~ 100 nm-thick films on the Zr<sub>31</sub>W<sub>55</sub>Si<sub>14</sub> at 100°C is approximately 10 times that on the Zr<sub>48</sub>W<sub>37</sub>Si<sub>15</sub>. The anodic oxide nanofilms consist of two layers, comprising a thin outer ZrO<sub>2</sub> layer and an inner ZrO<sub>2</sub>-WO<sub>3</sub>-SiO<sub>2</sub> layer. Both layers show thickness-dependent conductivity and the proton conductivity of the two-layer anodic films is enhanced one order of magnitude by reducing the film thickness from ~ 300 nm to ~ 100 nm. Different mechanisms are proposed for the thickness dependence of the conductivity of the outer and inner layers.



## **High Proton Conductivity in Anodic ZrO<sub>2</sub>–WO<sub>3</sub>–SiO<sub>2</sub> Nanofilms**

K. Ye, Y. Aoki, E. Tsuji, S. Nagata and H. Habazaki

ECS Transactions, **50**, 193-201 (2013)

The proton conductivity of the anodic ZrO<sub>2</sub>–WO<sub>3</sub>–SiO<sub>2</sub> nanofilms prepared by anodizing of sputter-deposited Zr<sub>37</sub>W<sub>47</sub>Si<sub>16</sub> alloy at several formation voltages for 1.8 ks in 0.1 mol dm<sup>-3</sup> phosphoric acid electrolyte at 20°C has been examined below 250°C in various environments. The proton conductivity activated by thermal treatment at 250°C is not influenced by the presence of O<sub>2</sub> and H<sub>2</sub>O in the atmosphere. However, the conductivity is enhanced by one order of magnitude in H<sub>2</sub>-containing atmosphere. The H<sub>2</sub>-induced conductivity enhancement is reversible; the enhanced conductivity is returned to an original value by exposing again in an O<sub>2</sub>-containing atmosphere.

## **Development and Application of High Durability Thermal Spray Material for Pulverized Coal Combustion Boiler**

S. Kyo, M. Nakamori, O. Ishibashi, and K. Kurokawa

Karyoku Genshiryoku Hatsuden, Supplement, 195-201 (2013)

Pulverized coal firing boilers have attained larger capacities, necessitating further effective environmental measures. Coal firing facilities implement measures to inhibit the generation of NO<sub>x</sub> by operating with low O<sub>2</sub> combustion. As a result, in the furnace, a low O<sub>2</sub> atmosphere forms due to the lack of oxygen, and sulfide corrosion takes place due to the relatively high pressure of H<sub>2</sub>S. In addition, damage is accelerated by multiple influences from the erosion damage due to steam blasts from the wall blower used to remove slag. Thermal spray coatings applied to the surface of boiler components such as heat exchanger tubes are effective for high temperature corrosion and erosion protection as those measures. This paper describes thermal spray coating for boiler components, laboratory test results and actual plants, and introduces boiler application examples. (In Japanese)

## **Effect of Boron on the Microstructure of Spark Plasma Sintered Ultrafine WC**

K. Nanda Kumar, Masaki Watabe, and Kazuya Kurokawa

Vacuum, **88**, 88-92 (2013)

The microstructure of sintered carbide compacts generally contain faceted and abnormally grown grains. In the present work we show the addition of a small quantity of boron to tungsten carbide powders can induce isotropic coarsening without any abnormal grain growth. The ability of boron to reduce faceting is brought about by the oxidation of boron at low temperatures which leads to isotropic wetting and roughening of particle boundaries during sinter-coarsening at elevated temperatures. Increase in boron content leads to enhanced grain growth and a limiting value to the boron concentration is suggested. Increase in the ambient pressure during sintering increases oxidation of boron and also the sintering temperature leading to a change in both grain shape and size. The isotropic coarsening behavior of WC in the presence of boron conforms to Jackson's theory of crystal growth based on the energetics of a rough liquid-solid interface.

## **Metal Disilicides as Ultra-High Temperature Oxidation Resistant and High-Temperature Corrosion Resistant Materials**

K. Kurokawa

*Materia*, **52**, 428-433 (2013)

High-temperature oxidation and High-temperature corrosion resistance of metal disilicides are reviewed. In this review, thermodynamics and mechanism of oxidation of various high metal disilicides were described, and the disilicides were classified in the view point of oxidation resistance or oxide scale structure. In addition, effective manner for the improvement of oxidation resistance were also suggested. Some of metal disilicides also show outstanding high-temperature corrosion resistance due to the formation of SiO<sub>2</sub> scale. This means SiO<sub>2</sub>-formers completely suppress the formation of sulfides and chlorides even in Na<sub>2</sub>SO<sub>4</sub>/NaCl-containing atmospheres. Based on the findings, utilization as coating materials are proposed. (In Japanese)

## **A Comparative Study of High Temperature Corrosion of $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ Forming Alloys in a $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$ Atmosphere**

Toto Sudiro, Tomonori Sano, Shoji Kyo, Osamu Ishibashi, Masaharu Nakamori,  
Kazuya Kurokawa

Oxid. Met., **80**, 589-597 (2013)

The present paper is designed to provide a summary of our study on the high temperature corrosion of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  forming alloys in the gas phase and liquid phase of  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  system by comparing their corrosion resistance at 1000 C. The obtained results show that the alumina-forming alloy experiences severe internal corrosion in the gas phase, compared with that in the liquid phase due to oxide cracking. This results in an increase in the inward diffusion and/or penetration of constituents of the salts and oxygen to form internal Al-oxide and Cr-sulfides. In the liquid phase, however, the formation of yttrium sulfide beneath a continuous double oxides layer of  $\text{Al}_5\text{Y}_3\text{O}_{12}$  and  $\text{Al}_2\text{O}_3$  may be related to the high affinity of yttrium for sulfur. On the other hand, it is apparent from the cross-sectional observations that a  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  forming alloys form a continuous and dense oxides layer, and demonstrate a high resistance against internal oxidation and corrosion in both corrosive environments.

## **Rapid fabrication of self-ordered porous alumina with 10-/sub-10-nm-scale nanostructures by selenic acid anodizing**

Osamu Nishinaga, Tatsuya Kikuchi, Shungo Natsui, and Ryosuke O. Suzuki

Sci. Rep., **3** 2748 (2013)

Anodic porous alumina has been widely investigated and used as a nanostructure template in various nanoapplications. The porous structure consists of numerous hexagonal cells perpendicular to the aluminum substrate and each cell has several tens or hundreds of nanoscale pores at its center. Because the nanomorphology of anodic porous alumina is limited by the electrolyte during anodizing, the discovery of additional electrolytes would expand the applicability of porous alumina. In this study, we report a new self-ordered nanoporous alumina formed by selenic acid ( $\text{H}_2\text{SeO}_4$ ) anodizing. By optimizing the anodizing conditions, anodic alumina possessing 10-nm-scale pores was rapidly assembled (within 1 h) during selenic acid anodizing without any special electrochemical equipment. Novel sub-10-nm-scale spacing can also be achieved by selenic acid anodizing and metal sputter deposition. Our new nanoporous alumina can be used as a nanotemplate for various nanostructures in 10-/sub-10-nm-scale manufacturing.

## **New n-type Silicide Thermoelectric Material with High Oxidation Resistance**

R. Funahashi, Y. Matsumura, T. Takeuchi, H. Tanaka, W. Norimatsu, E. Combe,  
R. O. Suzuki,

C. Wan, Y. Wang, M. Kusunoki and K. Koumoto,

Mater. Res. Soc. Symp. Proc. **1490** [1] (2013) 103-112.

In order to achieve waste heat recovery using thermoelectric systems, thermoelectric materials showing high conversion efficiency over wide temperature range and high resistance against oxidation are indispensable. A silicide material with good n-type thermoelectric properties and oxidation resistance has been discovered. The composition and crystal structure of the silicide are found out  $Mn_3Si_4Al_2$  (abbreviated as 342 phase) and hexagonal  $CrSi_2$  structure, respectively. Element substitution of Mn with 3d transition metals is succeeded. Enhancement of Seebeck coefficient is observed in a Cr-substituted sample. The maximum dimensionless thermoelectric figure of merit  $ZT$  is 0.3 at 573 K in air for the  $Mn_{2.7}Cr_{0.3}Si_4Al_2$  sample. Electrical resistivity of the  $Mn_3Si_4Al_2$  bulk sample holds constant value for 48 h at 873 K in air. This is due to formation of oxide passive layer on the surface of the bulk sample. The 342 phase is a promising n-type material with a good oxidation resistance in the middle temperature range of 500-800 K. [dx.doi.org/10.1557/opl.2013.117](https://doi.org/10.1557/opl.2013.117)

## **Growth Behavior of Anodic Porous Alumina Formed in Malic Acid Solution**

Tatsuya Kikuchi, Tsuyoshi Yamamoto, and Ryosuke O. Suzuki

*Appl. Surf. Sci.*, **284** (2013) 907-913.

The growth behavior of anodic porous alumina formed on aluminum by anodizing in malic acid solutions was investigated. High-purity aluminum plates were electropolished in  $\text{CH}_3\text{COOH} / \text{HClO}_4$  solutions and then anodized in 0.5 M malic acid solutions at 293 K and constant cell voltages of 200 - 350 V. The anodic porous alumina grew on the aluminum substrate at voltages of 200 - 250 V, and a black, burned oxide film was formed at higher voltages. The nanopores of the anodic oxide were only formed at grain boundaries of the aluminum substrate during the initial stage of anodizing, and then the growth region extended to the entire aluminum surface as the anodizing time increased. The anodic porous alumina with several defects was formed by anodizing in malic acid solution at 250 V, and oxide cells were approximately 300 - 800 nm in diameter.

## **Aluminum Bulk Micromachining through an Anodic Oxide Mask by Electrochemical Etching in an Acetic Acid / Perchloric Acid Solution**

Tatsuya Kikuchi, Yuhta Wachi, Masatoshi Sakairi, and Ryosuke O. Suzuki

Microelectronic Microengineering, **111** (2013) 14-20.

A well-defined microstructure with microchannels and a microchamber was fabricated on an aluminum plate by four steps of a new aluminum bulk micromachining process: anodizing, laser irradiation, electrochemical etching, and ultrasonication. An aluminum specimen was anodized in an oxalic acid solution to form a porous anodic oxide film. The anodized aluminum specimen was irradiated with a pulsed Nd-YAG laser to locally remove the anodic oxide film, and then the exposed aluminum substrate was selectively dissolved by electrochemical etching in an acetic acid / perchloric acid solution. The anodic oxide film showed good insulating properties as a resist mask during electrochemical etching in the solution. A hemicylindrical microgroove with thin free-standing anodic oxide on the groove was fabricated by electrochemical etching, and the groove showed a smooth surface with a calculated mean roughness of 0.2 - 0.3  $\mu\text{m}$ . The free-standing oxides formed by electrochemical etching were easily removed from the specimen by ultrasonication in an ethanol solution. Microchannels 60  $\mu\text{m}$  in diameter and 25  $\mu\text{m}$  in depth connected to a microchamber were successfully fabricated on the aluminum.



## **Deformation simulation of copper plates of slab continuous casting mold**

Xiang-ning Meng, Wei-ling Wang, Miao-yong Zhu, Ryosuke O. Suzuki

Proc. 4th International Symposium on High-Temperature Metallurgical Processing,

Edited by: Tao Jiang, Jiann-YangHwang, Phillip J. Mackey, Onuralp Yucel, and Guifeng Zhou,

TMS (The Minerals, Metals & Materials Society), (2013) 411-416.

A finite-element thermal-stress model of continuous casting mold is conducted to predict deformation of copper plates and its change with different cooling structure. The results show that deformation behavior of copper plates is mainly governed by cooling structure and thermalmechanical conditions, deformation amount is related to structure geometry, and a small deformation mutation occurs in cooper-nickel boundary due to different properties. The maximum deformation of hot surface centricities of wide face locate at 100 mm below meniscus and that of narrow face locate at meniscus and terminal of water slots and significant curvature fluctuations on both sides of copper-nickel boundary. The maximum deformation of centricities is increased up to 0.05 mm with thickness increment 5 mm of copper plates, and maximum deformations are only depressed 0.01 mm and 0.02 mm with increments of 1 mm nickel layer thickness and 2 mm water slot depth respectively.

## **Fabrication of a Meniscus Microlens Array Made of Anodic Alumina by Laser Irradiation and Electrochemical Techniques**

Tatsuya Kikuchi, Yuhta Wachi, Taka-aki Takahashi, Masatoshi Sakairi, and Ryosuke O. Suzuki

*Electrochim. Acta*, **94** (2013) 269-276.

An anodic alumina microlens array was fabricated by laser irradiation and electrochemical techniques. An aluminum specimen covered with a porous oxide film was irradiated with a pulsed Nd-YAG laser, and then electropolished to dissolve the aluminum substrate. A well-defined semi-elliptical micropore was formed on the aluminum by electropolishing. The immersion of the electropolished specimen in a  $\text{CrO}_3/\text{H}_3\text{PO}_4$  solution resulted in the dissolution of the remaining anodic oxide film. Subsequent re-anodizing enabled the formation of a characteristic meniscus-shaped oxide film on the micropore. A microlens array made of the thin anodic alumina film, which showed flexibility and heat resistance, was successfully fabricated by the lift-off of the anodic oxide.

## CO<sub>2</sub> Gas Decomposition to Carbon by Electro-reduction in Molten Salts

Koya Ohtake, Hiroshi Kinoshita, Tatsuya Kikuchi, and Ryosuke O. Suzuki

*Electrochimica Acta*, **100** (2013) 293-299.

The electrochemical decomposition of CO<sub>2</sub> gas in LiCl- Li<sub>2</sub>O or CaCl<sub>2</sub>-CaO molten salt was studied to produce carbon. This process consists of the electrochemical reduction of the oxide, Li<sub>2</sub>O or CaO, and the thermal reduction of CO<sub>2</sub> gas by metallic Li or Ca. Two kinds of ZrO<sub>2</sub> solid electrolytes were tested as an oxygen ions conductor and removed oxygen ions from the molten salts to the outside of reactor. After the electrolysis in the both salts, the aggregations of nanometer-scale amorphous carbon and rod-like graphite crystals were observed by transmission electron microscope. When 9.7% CO<sub>2</sub>- Ar mixed gas was blown into LiCl- Li<sub>2</sub>O or CaCl<sub>2</sub>- CaO molten salt, the current efficiency was evaluated to be 89.7% or 78.5%, respectively, by the exhaust gas analysis and the supplied charge. When the solid electrolyte with the better ionic conductivity was used, the current and the carbon production became larger. The rate determining step of this proposal was diffusion of oxygen ions in ZrO<sub>2</sub> solid electrolyte.  
[dx.doi.org/10.1016/j.electacta.2013.02.076](https://doi.org/10.1016/j.electacta.2013.02.076)

## Thermoelectric Generation Using Water Lenses

Ryosuke O. Suzuki, Atsushi Nakagawa, Hongtao Sui and Takeyuki Fujisaka

J. Electron. Mater., **42** (7) (2013) 1960-1965.

A solar light concentrator composed of water and plastic transparent film has been designed. This flexible lens design can trace the solar movement through control of the tensile stress and amount of water, and concentrate the solar energy onto the thermoelectric (TE) module surface. An experimental water lens was constructed, and the concentrated intensity was monitored by a photodiode as a function of  $x$ - $z$  position; For example, when 3.0 kg water was filled and tension of 69.0 N/m was applied to the transparent vinyl sheet, the concentration ratio was evaluated as the maximum of 28.0 at a depth of 657 mm from the water lens bottom surface. TE generation was tested to show the validity of the water lens. The surface condition of the receiver was found to be critical. [dx.doi.org/10.1007/s11664-013-2483-5](https://doi.org/10.1007/s11664-013-2483-5)

## **Design and Numerical Evaluation of Cascade-Type Thermoelectric Modules**

Takeyuki Fujisaka, Hongtao Sui and Ryosuke O. Suzuki

J. Electron. Mater., **42** (7) (2013) 1688-1696.

Thermoelectric (TE) generation performance can be enhanced by stacking several TE modules (so-called cascade-type modules). This work presents a design method to optimize the cascade structure for maximum power output. A one-dimensional model was first analyzed to optimize the TE element dimensions by considering the heat balance including conductive heat transfer, Peltier heat, and Joule heat, assuming constant temperatures at all TE junctions. The number of  $p-n$  pairs was successively optimized to obtain maximum power. The power output increased by 1.24 times, from 12.7 W in a conventional model to 15.7 W in the optimized model. Secondly, a two-dimensional numerical calculation based on the finite-volume method was used to evaluate the temperature and electric potential distributions. Voltage–current characteristics were calculated, the maximum power output was evaluated, and the efficiencies of two possible models were compared to select the optimal design. The one-dimensional analytical approach is effective for a rough design, and multidimensional numerical calculation is effective for evaluating the dimensions and performance of cascade-type TE modules in detail.

[dx.doi.org/10.1007/s11664-012-2400-3](https://doi.org/10.1007/s11664-012-2400-3)

## Formation of Niobium Powder by Electrolysis in Molten Salt

Isamu Ueda, Masahiko Baba, Tatsuya Kikuchi, and Ryosuke O. Suzuki

*Electrochimica Acta*, **100** (2013) 269-274.

Fine Nb<sub>2</sub>O<sub>5</sub> powder was filled into a basket-type cathode and immersed in molten CaCl<sub>2</sub>- 0.5 mol% CaO at 1173 K. Nb<sub>2</sub>O<sub>5</sub> immediately reacted with CaO in the molten CaCl<sub>2</sub> and formed calcium niobites that exhibited rod- or plate-like morphology. After the electrolysis of CaO with a graphite consumable anode, spherical particles of metallic niobium powder containing a residual oxygen concentration of 0.673 mass% O were obtained.

[dx.doi.org/10.1016/j.electacta.2013.01.054](https://doi.org/10.1016/j.electacta.2013.01.054)

## Thermoelectric properties of n-type $\text{Mn}_{3-x}\text{Cr}_x\text{Si}_4\text{Al}_2$ in air

R. Funahashi, Y. Matsumura, H. Tanaka, T. Takeuchi, W. Norimatsu, E. Combe,  
R. O. Suzuki, Y. Wang,

C. Wan, S. Katsuyama, M. Kusunoki, K. Koumoto

J. of Applied Phys. **112** (7), (2012) 073713.

A silicide material with a good n-type thermoelectric property has been discovered. This silicide possesses a composition of  $\text{Mn}_{3-x}\text{Cr}_x\text{Si}_4\text{Al}_2$  ( $0 \leq x \leq 0.7$ ) and hexagonal  $\text{CrSi}_2$  structure. The *a*- and *c*-cell parameters decrease with increasing the amount of Cr substitution. The absolute values of Seebeck coefficient and electrical resistivity increase by Cr substitution up to 573 K because of reduction of carrier density. The dimensionless thermoelectric figure of merit *ZT* reaches 0.21 at 773 K for a non Cr substituted sample at the Mn site and 0.30 at 573 K for a Cr substituted one with  $x=0.3$ . Since oxide passive layer is formed around the surface, electrical resistivity measured at 873 K is constant for 2 days in air, which indicates good oxidation resistance in air of this material. The  $\text{Mn}_{3-x}\text{Cr}_x\text{Si}_4\text{Al}_2$  is a promising n-type material with a good oxidation resistance in the middle temperature range. A thermoelectric module consisting of 64 pairs of legs has been fabricated using  $\text{MnSi}_{1.7}$  and non Cr substituted  $\text{Mn}_3\text{Si}_4\text{Al}_2$  devices as p- and n-type legs, respectively. Output power reaches 9.4 W, which corresponds to 2.3 kW/m<sup>2</sup> of power density against surface area of the substrate, for a heat source temperature of 873 K in air. [dx.doi.org/10.1063/1.4755793](https://doi.org/10.1063/1.4755793)

## **Production of Nb-Ti-Ni alloy in molten CaCl<sub>2</sub>**

Ryunosuke Enmei, Tatsuya Kikuchi and Ryosuke O. Suzuki,

*Electrochimica Acta*, **100** (2013) 257-260.

A Nb- Ti- Ni hydrogen permeable alloy was synthesized as a powder using the OS process, which involves the simultaneous reduction of a mixture of Nb, Ti, and Ni oxides by Ca that is generated from molten CaCl<sub>2</sub> via electrolysis. The mechanism confirmed that a BCC-(Nb, Ti) phase easily formed at an early stage of the reaction followed by the generation of a B2-TiNi phase from the lower oxides such as NbO and Ti<sub>2</sub>O. The oxygen content of the synthesized alloy decreased significantly to 0.27 mass% with increased electric charge. The three elements were uniformly distributed at the macroscopic level.

[dx.doi.org/10.1016/j.electacta.2012.11.044](https://doi.org/10.1016/j.electacta.2012.11.044)

## **Stable Mesh-free Moving Particle Semi-implicit Method for Direct Analysis of Gas-Liquid Two-Phase Flow**

Shungo Natsui, Hifumi Takai, Takehiko Kumagai, Tatsuya Kikuchi and Ryosuke O. Suzuki,

*Chemical Engineering Science*, **111** (2014) 286-298

This article presents a new particle-based numerical simulation scheme for gas-liquid flow. We improved the numerical stability, which is generally a problem with the particle method, and verified the model's accuracy for fundamental gas-liquid flow analysis. Because all the phases were discretized as particles in Moving Particle Semi-implicit (MPS) method, the proposed model can track the movement of both the gas and liquid phases directly. A large difference in the real density between the gas and liquid phases makes the gas-liquid interface behavior unstable. This study proposed an optimization of the weakly compressible Poisson equation, an initial particle arrangement, and a smoothed interface density in order to stabilize the multidensity flow analysis.

[dx.doi.org/10.1016/j.ces.2014.02.038](https://doi.org/10.1016/j.ces.2014.02.038)



## **Corrosion Inhibition by Zinc Corrosion Products on Zinc-Coated Steel**

Y. Sato and K. Azumi

*ECS Transactions*, **50** (47) 27-33 (2013).

The corrosion-inhibition of the iron covered with the corrosion products formed by dissolved zinc in the atmospheric corrosion was investigated by using a multichannel coupling current measurement technique. The coupling current map and coupling charge map of the partially covered iron electrode array in an arrangement of 10 x 10 were traced during the corrosion test. At the initial stage of corrosion test, iron was mainly protected by the sacrificial dissolution of metallic zinc and partially by the corrosion products of zinc precipitated on the iron surface. After complete depletion of metallic zinc, the iron surface covered with hydrozincite acted as cathode, while that covered with zincite layer acted as anode. The discrepancy between these two electrodes can be explained by the higher solubility of hydrozincite than that of zincite.

## **Evaluation of Micro Plasma Formed in the Narrow Gap in Electrolyte Solution**

H. Tamai, M. Hafner, A. Hassel, H. Tachikawa and K. Azumi

*ECS Transactions*, **50** (46) 85-91 (2013).

Microplasma was formed in a gap hole made in a quartz plate immersed in various kinds of electrolyte solutions at different concentrations. High-voltage AC was applied to the solution by using a pair of contact- or non-contact electrodes at both sides of the gap hole to ignite microplasma generation. Spectra of the light emitted from the microplasma showed elemental emission lines of the species contained in the solution, and their intensities depended on not only their concentration but also plasma conditions such as plasma temperature. A non-equilibrium plasma state was confirmed from estimated temperature of electrons and OH• radicals in the order of thousand and 10 thousand Kelvins. Deformation of the gap hole was observed depending on the polarization condition and species, probably due to high-temperature plasma and also dielectric loss in the gap hole.

## **Plating techniques to protect magnesium alloys from corrosion**

K. Azumi, H. H. Elsentriecy, J. Tang

in "Corrosion prevention of magnesium alloys", (Ed.) G-L Song, Woodhead Publishing Limited, Cambridge, UK (2013)

Plating on Mg alloys has been difficult issue due to their high susceptibility to the degradation reactions such as galvanic corrosion in the plating processes. In this chapter, surface conditioning, activation, electroless- or electro-plating methods are discussed from viewpoints of corrosion engineering. Degradation reactions of the Mg substrate in each plating stage are considered to figure out how to suppress degradation of substrate and to achieve uniform deposition of a plating layer. Building up an interface between the substrate and the plating layer is also an important subject to establish enough adhesion strength of the plating layer and low defect density to prohibit corrosion progress of the substrate. Al coating plating on Mg alloys electrodeposited from an ionic liquid bath is also introduced to provide coatings with less-galvanic coupling property with a less-noble Mg substrate.

## **Microelectrode Techniques for Corrosion Research of Iron**

K. Fushimi, Y. Takabatake, T. Nakanishi, Y. Hasegawa

*Electrochim. Acta*, **113** (2013) 741-745.

Two micro-electrode techniques, scanning electrochemical microscopy (SECM) and the micro-capillary cell (MCC) technique, were used to investigate corrosion behaviour of a polycrystalline iron surface in acidic sulphate media. Local corrosion reactivity was found to be strongly dependent on crystallographic orientation of the surface as well as measurement conditions. Results obtained by using microelectrode techniques are expected to reveal all aspects of corrosion behaviour of the surfaces of polycrystalline materials including iron.

DOI: 10.1016/j.electacta.2013.03.021

## **Microelectrochemistry of Dual-phase Steel Corroding in 0.1 M Sulfuric Acid**

K. Fushimi, K. Yanagisawa, T. Nakanishi, Y. Hasegawa, T. Kawano, M. Kimura

*Electrochim. Acta*, **114** (2012) 883-887.

Corrosion behavior of high-purity dual-phase carbon steel composed of only ferrite and martensite phases in 0.1 M sulfuric acid was investigated by both macro- and micro-electrochemical methods. The dual-phase steel corrodes non-uniformly due to galvanic coupling between its microstructures as well as self-corrosion of each phase. Hydrogen evolution reaction on galvanic-coupled martensite accelerates iron dissolution reaction of ferrite, though the corrosion rate of martensite was three-times larger than that of ferrite due to the self-corrosion in the acid. Totally, ferrite phases corrode selectively and the degree of selective corrosion was about two-times larger than martensite phases.

DOI: 10.1016/j.electacta.2013.09.162

## **Corrosion resistance of 9%Cr oxide dispersion strengthened steel in different electrolytic media**

S. Ningshena, M. Sakairi, K. Suzuki and S. Ukai

*Corrosion*, **69** (9), (2013), 863-874.

The corrosion resistance and passive film compositions of 9% Cr oxide dispersion-strengthened steel in different acidified and chloride media was evaluated. The results presented below show that with increasing concentrations of 1 M to 11.5 M nitric acid ( $\text{HNO}_3$ ), the open-circuit potential reveals a more noble potential, while in chloride-containing media, a less noble potential was observed. The potentiodynamic polarization plots exhibited higher breakdown/transpassive potentials in acidic media with 0.5 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and 1 M to 11.5 M  $\text{HNO}_3$ , and there was a shift in the corrosion potential toward the transpassive region as the  $\text{HNO}_3$  concentration increased from 1 M to 11.5 M. However, no intergranular corrosion attack was observed at the  $\text{HNO}_3$  concentrations studied. In acidic-chloride media (0.5 M  $\text{H}_2\text{SO}_4$  with 0.1 M and 0.5 M sodium chloride [ $\text{NaCl}$ ]) and in chloride only media (0.1 M  $\text{NaCl}$  and 0.5 M  $\text{NaCl}$ ) poor pitting corrosion resistance was attributable to the microstructural inhomogeneity and inclusions in the steel. The x-ray photoelectron spectroscopy analysis indicated that the passive film has iron(III) oxide ( $\text{Fe}_2\text{O}_3$ ) and chromium(III) oxide ( $\text{Cr}_2\text{O}_3$ ), along with yttrium oxide ( $\text{Y}_2\text{O}_3$ ). The scanning electron microscopy (SEM) examinations showed that the pits on the specimen were hemispherical and formed lace-like patterns. The corrosion properties affected by the dispersed oxide are also discussed in the paper.

## **Analysis of chemical compositions and morphology of surface films formed on 3003 aluminum alloy by immersion in different cation containing model tap waters**

M. Sakairi, K. Otani, A. Kaneko, Y. Seki and D. Nagasawa

Surface and Interface Analysis special Issue of ASST2012, **45** (2013), 1517-1521.

The effect of metal cations,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ , on oxide film structure and morphology changes during immersion corrosion tests of 3003 aluminum alloy in model tap waters was investigated by surface analysis techniques including Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy. The hardness of metal cations based on the hard and soft acids and bases (HSAB) concept was applied to explain the effect on the passive oxide film structure. Numerous nano-sized pits were observed after 86.4 ks immersion in model tap water, and nano-sized corrosion products were also observed especially in specimens immersed in  $\text{K}^+$  containing solutions. The AES and XPS results showed that hard metal cations like  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  were included in the oxide films, while soft metal cations were not included in the oxide films. The results are in good agreement with those which could be expected from the HSAB hardness of the metal cations.

## **Formation of alumina films with nano-dot structures by successive liquid phase deposition, anodizing, and substrate dissolution**

M. Sakairi, R. Fujita, H. Jha and T. Kikuchi

Surface and Interface Analysis special Issue of ASST2012, **45** (2013), 1510-1516.

A process based on successive anodizing, liquid phase deposition (LPD), re-anodizing, and aluminium substrate dissolution to form alumina films with nano-dot structures is demonstrated. Initially, a protective oxide film is formed on the aluminium surface to prevent further dissolution of the aluminium substrate during LPD processing. Because of heterogeneity in the protective oxide film, localized dissolution would otherwise occur under the film, resulting in pit formation during the LPD treatment. During re-anodizing, these pits act as a mold for anodic oxide resembling a nano-dot like structure. Optimization of LPD parameters, such as time and temperature, would make it possible to obtain alumina films with nano-dot structures with sizes smaller than 1  $\mu\text{m}$ . Alumina films with nano-dot structures with hollow can be realized by controlling the LPD conditions.

## **Formation of Nanoporous Structures on Planner Al-Zn Alloy Lining Layers by Anodic Oxidation**

M. Ishida, T. Ohmi, M. Sakairi and M. Igugchi

J. JSEM Special Issue, **13**(2013), s205-s208

We investigated the anodic oxidation of planner Al-Zn lining layer in a phosphoric acid solution to produce a nanoporous oxide film. The Al-Zn lining layer was produced by a sacrificial-core method using aluminum powder and zinc plate. No nanoporous structure was observed in the specimen after anodic oxidation at 50 V and 100 V for 7.2 ks. On the other hand, well-developed nanoporous structure was formed in the entire region in the case of 150 V for 7.2 ks or longer.

## **Effects of Alkali Leaching on Composition and Surface Structure of Cu-Al Alloy Layer Produced by Powder-Metallurgical Method**

A. Maruyama, T. Ohmi, M. Sakairi and M. Iguchi

J. JSEM Special Issue, **13** (2013), s194-s198.

In order to produce a Raney copper catalyst on the inner wall of microchannels, alkali leaching of Cu-Al alloy microchannel lining layers was investigated. Aluminum concentration of the lining layer decreased with leaching time when the lining-layer surface was exposed to a leaching solution. Furthermore, a fine copper structure was formed where aluminum was leached. This result indicates a possibility of fabrication of Raney copper catalyst.

## **The passive film characterization and anodic polarization behavior of 11% Cr ferritic/martensitic and 15% Cr oxide dispersion strengthened steels in different electrolytic solutions**

S. Ningshen, M. Sakairi, K. Suzuki and S. Ukai

Appl. Surf. Sci., **274**(2013), 345-355.

The ferritic/martensitic (F/M) and oxide dispersion strengthened (ODS) steels are the most promising candidate materials for future nuclear power plants. In the present work, the passive film compositions and its correlation with anodic polarization behavior of 11% Cr F/M and 15% Cr ODS steels was examined in different electrolytic solutions of borate buffer, acidic, acidified chloride and in chloride solution. The X-ray photoelectron spectroscopy analysis of the passive film reveals the existence of the layers of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  and in 15% Cr ODS steel along with  $\text{Y}_2\text{O}_3$ . The open circuit potential and potentiodynamic anodic polarization measurements show that pitting corrosion resistance is strongly dependent on electrolytic solutions and passive film compositions. The ODS steel indicated increased breakdown potential and wider passive range as compared to F/M steel in chloride containing media. In a non-chloride environment, this difference is not prominent. However, low pitting corrosion resistance of both steels in chloride solutions was attributable to  $\text{Cl}^-$  and microstructural inhomogeneity. The SEM micrographs of surface morphology of corrosion attack showed severe pitting corrosion attack in chloride solutions. The anodic polarization behavior of F/M and ODS steels in different electrolytic solutions was studied for this work in relation to passive film compositions.



## **Aluminum Bulk Micromachining through an Anodic Oxide Mask by Electrochemical Etching in an Acetic Acid / Perchloric Acid Solution**

T. Kikuchi, Y. Wachi, M. Sakairi, and R. O. Suzuki

Microelectronic Engineering, **111** (2013), 14-20.

A well-defined microstructure with microchannels and a microchamber was fabricated on an aluminum plate by four steps of a new aluminum bulk micromachining process: anodizing, laser irradiation, electrochemical etching, and ultrasonication. An aluminum specimen was anodized in an oxalic acid solution to form a porous anodic oxide film. The anodized aluminum specimen was irradiated with a pulsed Nd- YAG laser to locally remove the anodic oxide film, and then the exposed aluminum substrate was selectively dissolved by electrochemical etching in an acetic acid/perchloric acid solution. The anodic oxide film showed good insulating properties as a resist mask during electrochemical etching in the solution. A hemicylindrical microgroove with thin free-standing anodic oxide on the groove was fabricated by electrochemical etching, and the groove showed a smooth surface with a calculated mean roughness of 0.2–0.3  $\mu\text{m}$ . The free-standing oxides formed by electrochemical etching were easily removed from the specimen by ultrasonication in an ethanol solution. Microchannels 60  $\mu\text{m}$  in diameter and 25  $\mu\text{m}$  in depth connected to a microchamber were successfully fabricated on the aluminum.

## **Fabrication of a Meniscus Microlens Array Made of Anodic Alumina by Laser Irradiation and Electrochemical Techniques**

T. Kikuchi, Y. Wachi, T. Takahashi, M. Sakairi and R. Suzuki

*Electorchimica Acta*, **94** (2013), 269-273.

An anodic alumina microlens array was fabricated by laser irradiation and electrochemical techniques. An aluminum specimen covered with a porous oxide film was irradiated with a pulsed Nd-YAG laser, and then electropolished to dissolve the aluminum substrate. A well-defined semi-elliptical micropore was formed on the aluminum by electropolishing. The immersion of the electropolished specimen in a  $\text{CrO}_3/\text{H}_3\text{PO}_4$  solution resulted in the dissolution of the remaining anodic oxide film. Subsequent re-anodizing enabled the formation of a characteristic meniscus-shaped oxide film on the micropore. A microlens array made of the thin anodic alumina film, which showed flexibility and heat resistance, was successfully fabricated by the lift-off of the anodic oxide.

## **Corrosion Study and Passive Film Characterization of 11%Cr F/M and 15%Cr ODS Steels**

M. Sakairi, S. Ningshen, K. Suzuki and S. Ukai

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An oxide dispersion strengthened steels (ODS) are one of the most notable structural materials being developed for future high-temperature energy production technologies, and several studies have been devoted to the development of ODS materials for such applications. However, only little paper focuses on corrosion behavior of ferritic martensitic (F/M) and ODS steels. The corrosion behavior of 11%Cr F/M steel and 15%Cr ODS steel were evaluated using electrochemical methods in borate buffer and  $1\text{kmol m}^{-3}$   $\text{HNO}_3$  with or without NaCl and also in boiling 60% nitric acid. The corrosion resistance results clearly indicated the influences of steel alloys composition and chloride ions. The XPS results of the pre-passivated surface revealed that the oxide formed were composed predominantly of  $\text{Fe}_2\text{O}_3$  along with  $\text{Cr}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$  layers in ODS steel. The corrosion rate measured in boiling nitric acid for 48h for both the steels shows high corrosion rate in boiling condition. The SEM observation of the pit morphology after corrosion tests appears with shallow pit in both steel surfaces. The corrosion degradation behavior in relation to the composition of the passive oxide film in different electrolytic solutions is discussed in this paper.

## **Formation of area and thickness controlled porous type aluminum anodic oxide films by Sf-MDC**

M. Sakairi, T. Yamaguchi, T. Murata and K. Fushimi, ECS Transaction

ECS Trans., **50**(37) 255-262 (2013)

The solution flow type micro-droplet cell (Sf-MDC) was applied to local anodizing for formation of thickness and width controlled porous type aluminum oxide films. The effect of substrate temperature and repetition number of droplet on the film formation behavior was investigated. Formed oxide film thickness increased with both increasing substrate temperature and repetition number. The current during anodizing decreases with inverse of substrate temperature. Controlling the substrate temperature and the repetition number make it possible to form area and thickness controlled porous type aluminum anodic oxide films.

## **Corrosion Resistance of 9 - 15% Cr ODS steels and its Comparison with Austenitic Stainless Steel**

S. Ninghsen, M. Sakairi, K. Suzuki and S. Ukai

Advanced Materials Research, **794** (2013), 575-582.

An oxide dispersion strengthened steels are one of the most promising high temperatures, and high performance advanced structural material being developed for future fast reactors and high-temperature Generation IV reactors. In the present work, the corrosion resistance and its correlation with the passive film compositions of 11% Cr F/M and 9-15% Cr (with Zr or Hf) ODS steels is examined and compared with AISI type 304L stainless steel in boiling 60 - 62% (~13 M) HNO<sub>3</sub>. The corrosion rate measured in 62% HNO<sub>3</sub> for 240 h of 11% Cr F/M, 9% Cr and 15% Cr (Zr) ODS steels show high corrosion rate. On the other hand, low corrosion rate was observed in 304L stainless steel (0.21 to 23 mm y<sup>-1</sup>). However, severe intergranular corrosion attack was revealed in type 304L SS after 240 h exposure, but none in ODS steels. Such an intergranular corrosion attack seen in type 304L stainless steel is undesirable. On the contrary, low corrosion rate (0.04-0.15 mm y<sup>-1</sup>) of 15% Cr (Hf) ODS steel in 3 M, 6 M and 9 M HNO<sub>3</sub>, comparable to that of type 304L stainless steel was observed. The improved corrosion resistance of 15% Cr (Hf) ODS steel was attributed to enrich (20 at. %) and protective Al<sub>2</sub>O<sub>3</sub> layer formation in addition to Cr<sub>2</sub>O<sub>3</sub> in the passive film.

## **Effect of the metal cations in model tap water on corrosion behaviour and passive film structure of Al**

M. Sakairi, K. Otani, R. Sasaki, A. Kaneko, Y. Seki, D. Nagasawa

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The effect of metal cation on corrosion behaviour and passive film structure of highly pure aluminium in model tap water was examined by immersion corrosion tests and X-ray photoelectron spectroscopy (XPS). A hardness of metal cation, which was based on hard acid and soft base concept, was employed to explain the effect of metal cations. The total mass change after 30 days decrease with increasing added metal cation's hardness. Hard metal cations in the solution may incorporate in the passive film and inducing film structure changes.

## **Effect of sodium acetate in model oil and gas environments on oxide film structure and corrosion behavior of 13%Cr stainless steel**

M. Sakairi, A.Kikawa, S. Hashizume, T. Taniguchi

Proc. of NACE-EAP 2013, EAP13-4605 (2013)

The effect of acetate ions on structure of surface oxide films and corrosion behavior was investigated by X-ray photoelectron spectroscopy (XPS) and electrochemical techniques. A 13% Cr stainless steels with 0.2% C was used as samples, and pH controlled 25 mass% NaCl with 0 to 40.0 g dm<sup>-3</sup> CH<sub>3</sub>COONa at different temperature were used as model environments. From polarization measurements, pitting potential decreases with increasing CH<sub>3</sub>COONa concentration, however, more addition of it, pitting potential increases with increasing the concentration. From XPS analysis, intensity ratios of both Fe<sup>0</sup> and Cr<sup>0</sup> decrease with increasing CH<sub>3</sub>COONa, more addition of CH<sub>3</sub>COONa, these increase with increasing its concentration. The intensity ratio of OH<sup>-</sup> increases with increasing CH<sub>3</sub>COONa concentration at low concentration, more addition of CH<sub>3</sub>COONa it decreases with increasing its concentration.

## **Corrosion and Protection of Aluminum (2)- Corrosion behavior of aluminum change with metal cations in model tap water**

M. Sakairi, K. Otani A. Kaneko, Y. Seki and D. Nagasawa

Rust prevention and control Japan, **57**, 4 (2013), 147-153. (Japanese)

The corrosion behavior of aluminum is strongly depended on chloride ion concentration, however, the metal cation also influence on the corrosion rate of the aluminum in tap waters. In this paper reported effect of metal cation on galvanic corrosion behavior of pure aluminum. The hardness of metal cations based on the hard and soft acids and bases (HSAB) concept was applied to explain the results.

## **A Combined Hot Dip Aluminizing/Laser Alloying Treatment to Produce Iron-Rich Aluminides on Alloy Steel**

M. Emami, H.R. Shahverdi, S. Hayashi, M.J. Torkamany

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In the present study, a two-step surface treatment was employed to produce an iron-rich aluminide surface layer on 9Cr1Mo steel. In the first step, the steel specimen was immersed in a 1073 K (800°C) aluminizing bath for 90 seconds to obtain an Al-rich iron aluminide/Al double layer. Then, the aluminum-rich layer and some portion of the substrate material underneath were melted using a pulsed Nd:YAG laser with different pulse energies in the range of 4 to 8 J. The surface and cross section of the alloyed layers were studied using optical microscopy, scanning electron microscopy, an electron microprobe, and X-ray diffraction analyses. The results showed that after laser remelting of the hot dipped aluminized steel at a pulse energy of 7 J, an integrated layer of FeAl replaced the primary layer..



## **The Mechanism of Phase Transformation in Thermally Grown FeO Scale Formed on Pure-Fe in Air**

S. Hayashi, K. Mizumoto, S. Yoneda, Y. Kondo, H. Tanei, S. Ukai

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The isothermal phase transformation behavior of thermally grown oxide scale of FeO, which was formed on Fe at 700 °C in air for 16 min, was investigated at 320, 450, 500, 520, and 560 °C in air. The phase transformation of FeO was found to consist of four transformation modes: (1) growth of outer Fe<sub>3</sub>O<sub>4</sub> layer; (2) precipitation of Fe<sub>3</sub>O<sub>4</sub>; (3) formation of magnetite seam; and (4) eutectoid decomposition of FeO. The transformation was always completed by the eutectoid decomposition at all temperatures in the present study; however, the proportion of transformation mode (1) and (2) strongly depended on temperature. At higher temperatures growth of the outer Fe<sub>3</sub>O<sub>4</sub> layer initially predominates, but the precipitation of Fe<sub>3</sub>O<sub>4</sub> controls the initial transformation at lower temperature before the eutectoid reaction. The eutectoid reaction was found to be initiated by Fe nucleation from Fe-saturated FeO. Fe saturation in FeO was due to growth and/or precipitation of Fe<sub>3</sub>O<sub>4</sub> and formation of the magnetite seam layer, which acts as a diffusion barrier for Fe inward diffusion into Fe substrate. It was proposed that these transformation modes, growth and/or precipitation of Fe<sub>3</sub>O<sub>4</sub> and magnetite seam formation, are necessary to begin the eutectoid reaction, i.e., completion of FeO scale transformation.

## High Temperature Performance of an FeAl Laser Coated 9Cr1Mo Steel

M. Emami, S.M.M. Hadavi, S. Hayashi, H.R. Shahverdi,

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The isothermal high temperature corrosion behavior of an FeAl coating, coated on 9Cr1Mo steel through laser surface alloying, was studied in atmospheres of pure oxygen and  $O_2+1\%SO_2$ . The specimens were tested at 500, 600, and 700°C for 4-100 h. The mass change of the specimens versus time of exposure was used to study the kinetics of oxidation. The coating degradation through interdiffusion of alloying elements between the surface layer and substrate was investigated by long-term oxidation tests in air. OM, SEM, FESEM, EDS and EPMA analyses were used to study the oxidation behavior of the intermetallic coating. The results showed excellent oxidation/sulfidation resistance of the coated material due to a negligible growth rate of the oxide scale. However, the coating was degraded because of the interdiffusion of Al and Fe atoms between the coating and substrate after prolonged exposure to elevated temperatures.

## Various Factors Affecting Al<sub>2</sub>O<sub>3</sub> Scale Transformation

S. Hayashi

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Effect of various factors on the metastable to stable phase transformation behavior of a thermally grown oxide scale of Al<sub>2</sub>O<sub>3</sub> was reviewed and discussed on the basis of the results obtained from our recent studies. In this paper, among the factors affecting this phase transformation, particular attention has focused on the effect of Fe in order to understand the different phase transformation behavior of Al<sub>2</sub>O<sub>3</sub> scale formed on different alloy systems in different oxidation environments. In order to explore the effect of Fe on the phase transformation, the oxidation behavior of various Al<sub>2</sub>O<sub>3</sub> forming Fe-based model alloys was systematically investigated. The development of different oxide scales on different alloys during a high-temperature oxidation, including the initial transient stage of oxidation followed by isothermal oxidation in different oxidation atmospheres, was examined by in-situ X-ray diffraction by means of the Synchrotron radiation. Fe was found to accelerate the phase transformation to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This effect can be considered to be due to an initial formation of Fe<sub>2</sub>O<sub>3</sub>, which is an isomorphous crystal structure with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Further contributing factor of Fe on the transformation can be a doping of Fe<sup>3+</sup> ion, which formed during an initial transient oxidation stage, in the Al<sub>2</sub>O<sub>3</sub> scale. The oxidation atmospheres are considered to indirectly affect the phase transformation by changing in the formation behavior of Fe<sub>2</sub>O<sub>3</sub> and (Al, Fe)<sub>2</sub>O<sub>3</sub> solid solution during an initial transient oxidation stage

