9th International Conference on the Physical Properties and Application of Advanced Materials

14-18 September 2014, Krakow, Poland

Programme and Abstracts

9th ICPMAT Krakow 2014

9th International Conference on the Physical Properties and Application of Advanced Materials

ICPMAT2014

14-18 September 2014

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Editor: K. Przybylski

AGH University of Science and Technology

Krakow, September 2014

Welcome to the 9th International Conference on the Physical Properties and Application of Advanced Materials (ICPMAT2014)! This conference is organized by the “Krakus” Foundation of AGH under the scientific patronage of the Faculty of Materials Science and Ceramics, AGH University of Science and Technology. The conference covers fundamental and applied research and current developments within physics and materials science, including structural materials, functional materials, advanced characterization techniques and computational materials science. Structural materials include light metals, steels, alloys and deformation. Functional materials involve superconductors, oxides, ceramics, spintronics, energy-related materials and nanomaterials. Advanced characterization techniques involve techniques such as electron microscopy and muon studies. Computational materials science includes density functional theory studies.

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ICPMAT2014

Held under the Auspices of
the President of the Krakow Branch of Polish Academy of Sciences
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Scientific Programme

Sunday, 14th September

18:00 **Welcome reception and dinner** (Hotel POLONEZ – Reymonta street 15)

Monday, 15th September

Opening ceremony (Lecture Room 0.10B, Building B-8)

9:00-9:10 **Kazimierz Przybylski**
Welcome

9:10-9:20 **Jerzy Lis (DEAN)**
Opening Remarks

9:20-9:30 **Yuukou Horita (DEAN)**
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13:00-18:00 *Technical Tour to Salt Mine Museum in Wieliczka*

18:30 *Dinner*

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ABSTRACTS

PROCESSING AND PROPERTIES OF MAX PHASES – BASED MATERIALS USING SHS TECHNIQUE

J. Lis[1], R. Chlubny[1], C. Kapusta[2]

**[1]AGH University of Science and Technology
Faculty of Materials Science and Ceramics;
[2]AGH University of Science and Technology
Faculty of Physics and Applied Computer Science**

Authors present results of works on the interesting new group of advanced ceramics called MAX phases – Ti-based ternary carbides and nitrides. They have an original layered structure involved highly anisotropic properties laying between ceramics and metals, with high elastic modulus, low hardness, very high fracture toughness and high electrical and heat.

Using Self-Propagating High-Temperature Synthesis (SHS) in the combustion regime it is possible to prepare MAX phases-rich powders that can be used as the precursors for preparation of dense MAX polycrystals by presureless sintering or hot-pressing. Different novel Ti-based phases with layered structures, namely: Ti_3AlC_2, Ti_3AlC, Ti_2AlC and Ti_2AlN have been synthesized in a combustion regime. The possibility of controlling of combustion phenomena for obtaining near single-phase products is discussed in details as well as some of properties of the materials tested as structure and functional ceramics.

ANALYTICAL STEM AND ITS APPLICATION TO THIN FILM CHARACTERIZATION

Masahiro Kawasaki[1], Masateru Nose[2], Makoto Shiojiri[2.3]

[1]JEOL US, [2]Univ. of Toyama, [3]Kyoto Inst. of Tech.

Analytical scanning transmission electron microscopy (STEM) is indispensable for investigation and characterization of nanoscale novel materials and devices. First, we present briefly the history of STEM,[1, 2] and instruct the characteristics of the STEM imaging, in particular, of high-angle annular dark-field (HAADF), comparing with conventional transmission electron microscopy.[3,4] Next, our recent STEM investigations on Au/TiO_2 thin films deposited on the glass substrate[5] and multilayered Cr(Al)N/SiO*x* nanocomposite coatings[6,7] are reviewed as examples of characterization of thin films.

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2. A. Crewe, Scanning electron microscopes: Is high resolution possible? Science **154,** (1966) 279-738.
3. M. Shiojiri and H. Saijo, Imaging of high-angle annular dark-field scanning transmission electron microscopy and observations of GaN-based violet laser diodes. J. Microsc. **223,** (2006) 172-17.
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7. M. Kawasaki, M. Nose, I. Onishi, and M. Shiojiri, Structure of multilayered Cr(Al)N/SiO_x nanocomposite coatings fabricated by differential pumping co-sputtering. Appl. Phys. Lett. **103**, (2013) 201913 (4 pages).

HEXAGONAL EQUILIBRIUM PHASE IN Al-Mg_2Si ALLOYS WITH NOVEL ELEMENTS

Kenji Matsuda[1], Susumu Ikeno[2]

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[2]Hokuriku Polytechnic College, 1289-1 Kawaberi, Uozu, Toyama, 930-0856 Japan

Al-Mg-Si alloy has the equilibrium phase of β-Mg_2Si which is a square platelet and the orientation relationship of $\{001\}_\beta$ //$\{001\}_m$. The other shape and orientation relationship have been found out by our research. It is a hexagonal platelet and the orientation relationship of $\{111\}_\beta$ //$\{111\}_m$. This phase appears the specific condition of alloy and aging condition. For example, Cu, Ag or Au added alloy shows this hexagonal phase and it has the same crystal structure as a normal β-Mg_2Si in Al-Mg_2Si alloy without additional element. In this presentation, I will introduce the study for this phase by TEM and SEM in detail.

THE EFFECT OF EVALUATION OF MICROSTRUCTURE ON CORROSION RESISTANCE OF ANNEALED Ni–P AMORPHOUS ALLOYS

Yong Zou, Guanlin Zhao, Jie Chen

Key Lab of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University, Jinan 250061, Shandong, China

Amorphous Ni–P alloys were prepared via electroless plating and annealing at low temperature at different times to obtain different microstructures. The local atomic structure of annealed Ni–P amorphous alloys was analyzed by calculating the atomic pair distribution function from the XRD patterns. When annealing temperature is 250°C, corrosion resistance in 0.5 M H_2SO_4 was investigated via electrochemical techniques. The results indicated that the improvement of corrosion resistance is in agreement with decreasing order cluster size. The order cluster size of annealed Ni–P amorphous alloys initially decreased then increased with increasing annealing time. By contrast, corrosion resistance showed an opposite trend. The more results will be reported in conference.

THE DISCOVERY OF THE REVERSE FCC DEFORMATION TWINNING

M.S. Szczerba[1], S. Kopacz[1], M.J. Szczerba[2]

[1]Department of Materials Science and Non-Ferrous Metals Engineering, AGH University of Science and Technology, Krakow, Poland;
[2]Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Krakow, Poland

The discovery of the reverse FCC deformation twinning is reported. On the basis of the obtained experimental results, on FCC twin/matrix lamellae single crystal structures generated during tension and then subjected to secondary compression deformation path, the exact equivalence of the $C = C^{-1}$ was found, where C and C^{-1} are the correspondence matrix and its reciprocity, respectively. In particular, following the experimental results, obtained after X-ray and electron microscopy/electron backscatter diffraction experimental techniques, it was proved that the formation of kink bands during the compression deformation is totally controlled by the reverse mode of FCC twinning. Also a large difference between the C and C^{-1} twinning stress was found - the latter being lower by about factor of two – to be responsible for the tensile-compression asymmetry of the yield stresses. This discovery should find important applications in theory and modeling of large plastic deformation phenomena of FCC materials, including cycling deformation phenomena as well as the mechanical anisotropy of twin/matrix systems. Finally, very recently published papers, related to the discovery of the reverse FCC deformation twinning, are also discussed.

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AN Al-Zn-Mg-Cu ALLOY PRODUCED BY GRAVITY CASTING PROCESS

Seiji Saikawa[1], Goshi Aoshima[2], Susumu Ikeno[3], Keisuke Morita[4], Noboru Sunayama[4], Koichi Komai[4]

[1]Graduate School of Science and Engineering for Research, University of Toyama;
[2]Graduate School of Science and Engineering for Education, University of Toyama;
[3]Hokuriku Polytechnic College;
[4]Tanida Ltd

High-strength aluminum alloy are widely used for structural components in aerospace, transportation and racing car applications. The objective of this study is to enhance the strength of the Al-Zn-Mg-Cu alloy used for gravity casting process. All alloys cast into stepped- form sand mold (Sand-mold Casting; SC) and Y-block shaped metal mold (Permanent mold Casting; PC), and then two –step aged at 398-423K after solution treated at 743K for 36ks. The tensile strength and total elongation of the two-step aged SC alloys were 353-387MPa and about 0.4% respectively. This low tensile properties of the SC alloys might be caused by remaining of undissolved crystallized phase such as Al2CuMg and Al-Fe-Cu system compounds. However, good tensile properties were obtained from PC alloys, tensile strength and 0.2% proof stress and elongation were 503-537MPa, 474-519MPa and 1.3-3.3%. The reason of the good properties in PM alloys, amount of undissolved crystallized phase became lower than that of SC ones and primary crystallized alpha-Al phase was changed finer, due to high cooling rate at solidification in casting.

NATURAL AGING IN A FRICTION STIR WELDED HEAT TREATABLE ALUMINUM ALLOY

Izabela Kalemba[1], Carter Hamilton[2], Stanislaw Dymek[1]

[1]Faculty of Metal Engineering and Industrial Computer Science, AGH University of Science and Technology;
[2]Department of Mechanical and Manufacturing Engineering, Miami University, School of Engineering and Applied Science, USA

The long term natural aging behavior of friction stir welded aluminum 7136-T76 extrusions was investigated. The microstructural characteristics and mechanical properties in the as-welded, three years naturally aged and six years naturally aged conditions were studied and correlated to a coupled thermal/material flow model of the joining process. Hardness profiles taken along the mid-plane thickness of the workpiece displayed the characteristic W-shape typical to friction stir welded aluminum alloys. In the as-welded condition, however, the profile was skewed to the advancing side, such that the advancing side hardness was lower than that on the retreating side. With natural aging, hardness recovery occurred on both sides of the weld, but the position of the hardness minima, particularly on the advancing side, shifted away from the weld centerline. The shape of the hardness profile could be correlated to the temperature distribution predicted by the numerical model. The numerical simulation demonstrated that the temperature profile is also skewed to the advancing side with greater processing temperatures occurring on this side of the weld. When compared to the dissolution temperature of the equilibrium phases, the extent of dissolution was greater on the advancing side and occurred to a greater distance from the centerline than on the retreating side. The hardness behavior upon natural aging, therefore, correlated to the temperature profile developed during welding and the degree to which phase dissolution occurred in the regions adjacent to the stir zone. The hardening effect in the stir zone resulting from the natural aging was associated with the nucleation of the large volume fraction of GP precipitates.

EFFECTS OF DOUBLE SOLUTION TREATMENT AND AGE HARDENING ON MICROSTRUCTURE, HARDNESS AND CORROSION RESISTANCE OF CAST Al-Si-Cu ALLOY

Amporn Wiengmoon[1], Piyaporn Sukchot[1], John T.H. Pearce[2], Torranin Chairuangsri[3]

[1]Department of Physics, Faculty of Science, Naresuan University, Thailand;
[2]National Metal and Materials Technology Center, Thailand;
[3]Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Thailand

Effects of double solution treatment and age hardening on microstructure, hardness and corrosion resistance of cast A319 (Al-4.93wt%Si-3.47wt%Cu) alloy were investigated. The first solution treatment was performed at 500 ± 5°C for 8 hours, while the second solution treatment was done in the temperature range of 510 to 530 ± 5°C for 2 hours, both followed by quenching in hot water at 80°C. Artificial T6 aging after solution treatment was performed at 170°C for 24 hours. The results revealed that the as-cast microstructure consists of primary dendritic α-Al, eutectic Si and intermetallic phases (Al_2Cu and Al_5FeSi). Dissolution and spheroidization of the intermetallic phases can be enhanced by double solution treatment. TEM results revealed that the precipitate after age hardening is Al_2Cu. Potentiodynamic and hardness tests revealed that, after double solution treatment and aging, the corrosion current was decreased, while the alloy hardness was comparable as compared to those in the case of single solution treatment and aging. Even though economic feasibility is to be evaluated, double solution treatment seems promising for improvement of corrosion resistance of the cast A319 alloy.

CAVITATION WEAR OF STRUCTURAL CERAMICS AND THEIR COMPOSITES

Zbigniew Pedzich

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Cavitation is a phenomenon caused by the repeated nucleation, growth, and violent collapse of clouds of bubbles within the liquid. Microstreams of liquid developed during the implosion of cavitation bubbles as well as the action of pressure waves from disappearing bubbles are the main causes of destruction on swilled surfaces leading to a loss of material, i.e. to cavitation erosion. The usage of ceramic materials in applications endangered by intensive cavitation could significantly limit corrosion phenomena. In the presented work, cavitation erosion resistance of commonly used, in structural applications, oxide phases (alumina, tetragonal zirconia, silicon carbide, silicon nitride) were investigated. Additionally, the behaviour under cavitation conditions of a few ceramic composites based on oxide matrices was tested. Phenomena influencing cavitation wear at each stage of development were recognized and described.

EBSD OF EQUAL CHANNEL ANGULAR PRESSED Al-Zn-In SACRIFICIAL ANODE

Chaiyasit Banjongprasert[1], Chonlada Domrong[1], Toranin Chairuangsri[2]

[1]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Thailand; [2]Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, Thailand

Equal Channel Angular Pressing (ECAP) is one of Severe Plastic Deformation (SPD) processes. The process can give a high strain and lead to ultrafine-grained structure. This study will investigate the effects of severe plastic deformation on the microstructure of an Al-Zn-In sacrificial anode. The Al-Zn-In samples with a diameter of 20mm and 100mm long were pressed with an ECAP die with pressing angle of 100˚ using Route Bc. The grain size was reduced with a number of pressing pass from more than 100μm to several μm after ECAPing for 4 passes. Electron Backscattered Diffraction (EBSD) was used to characterize the grain size and the effects of high strain on misorientation and textures. It was found that not only smaller grain size severe plastic deformation also provided a refinement of particles in the microstructure. This was favorable due to a more uniform corrosion in the Al-Zn-In sacrificial anode and led to a longer lifetime in service conditions. The details of microstructure features will be addressed in the paper.

THE EFFECT OF σ PHASE ON CORROSION BEHAVIOR OF DUPLEX STAINLESS STEEL F55

Kento Ejiri[1], Jyunichi Hirabayashi[2], Satoshi Matuoka[2], Yuichi Yamamoto[2], Masahico Hatakeyama[3], Satoshi Sunada[3]

[1]Graduate School of Science & Engineering for Education, University of Toyama, Japan; [2]PACIFIC STEEL MFG; [3]Graduate School of Science & Engineering for Research, University of Toyama, Japan

Duplex stainless steel can be used in harsh environments, because of its excellent strength and corrosion resistance. However, precipitate of σ phase, which degrade the corrosion resistance is formed during fabrication. Precipitate of σ phase formed significantly in the temperature range of 1073 K ~ 1173 K. To clarify the mechanism of degradation in corrosion resistance, we prepared the three kinds of duplex stainless steels (F55), which have different volume fraction of σ phase. The duplex stainless steels were heat treated at 1373 K, 1173 K and 1273 K, respectively. Amount of σ phase decreases with the heat temperature increases, and it does not form at 1373 K. Result of the polarization curves measured on these specimens, shows similar tendency in the properties of the polarization curves. The corrosion potential decreased with increase of amount of the σ phase. Thus the corrosion rate shows positive correlation with amount of σ phase. Next, we carried out constant potential test using a specimen, which was heat treated at 1173 K and containing a large amount of σ phase. After etching, the tissue, which seems to be undissolved σ phase was observed by optical microscope. X-ray diffraction results shows that the peak of σ phase after constant potential test relatively increased to that of α phase. Therefore the tissue was confirmed as σ phase on α phase. Since, it shows small corrosion potential (large corrosion rate) compared to the specimen without σ phase, formation of σ phase enhanced the anode reaction. Hence, it is evident that the α phase, which surround the σ phase, is easily dissolved.

FRICTION STIR WELDING OF DISIMILAR ALUMINUM ALLOY SHEETS UNDER TEMPERATURE GRADIENT

Toshiya Shibayanagi[1], Kenshi Takahata[2], Makoto Takahashi[3], Kenji Ikeuchi[2]

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The present work tries to experimentally prove that the temperature gradient is effective for producing sound dissimilar joints by Friction Stir Welding (FSW). FSW is a novel joining method developed in TWI, UK aiming at the joining of aluminum alloys followed by lots of intensive works expanding its applications to the other metals such as copper, titanium, steels. FSW is based on a high temperature deformation in the vicinity region around the welding tool rotating with a high speed. The deformation process is called `metal flow` and this is the key to optimize the yielding microstructure in the joints. The metal flow strongly depends on temperature, thus dissimilar joining by FSW should be discussed with the temperature distribution in the metals being welded. The present work utilized commercially pure aluminum and 2024-T3 aluminum alloy sheets of which deformation characteristics are different from each other. The FSW tests were carried out by cooling the pure aluminum side with a liquified nitrogen so that both materials possess similar flow stresses during welding. Joints with defects were produced without the cooling unit, and insufficient metal flow was observed on the cross section of the joints. On the contrary the cooling method realized sound joints with few amount of voids that is attributed to a sufficient metal flow. Therefore, control of temperature distribution in the workpieces is a promising way to produce sound dissimilar joints by FSW.

RECENT STUDIES BY SURFACE COATING GROUP IN UNIVERSITY OF TOYAMA

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The surface and coatings laboratory was established in 1996 and study of surface coatings has been carried on by collaborations with many researchers for almost two decades. When the author got joint assignment of “Graduate School of Science & Engineering” and “Faculty of Art & Design” in 2012, the “Surface Coatings Laboratory” was relocated within the “Laboratory of Controlling for Nano/Micro Structure of Materials” in association with Prof. Matsuda and other professors in the department of materials science and engineering.

Today, there are two category of research in this laboratory: one is the field of hard coatings, the other is the functional material films. In the former field, nanocomposite coating of a transition metal nitride and boron nitride such as TiAlN/BN or CrAlN/BN have been studied. The latter one exhibits a special characteristic of self-hardening phenomenon by annealing in air. Hard coatings consisting of ubiquitous elements are also investigated. AlN/SiCN coatings have high hardness of 30~38 GPa and thermal expansion coefficient similar to that of steel, and self- hardening characteristics. For the study of these coatings, combination of HR-TEM and XPS is the most powerful tool. TEM micrographs showed a disruption in the columnar structure by a very thin layer (20 ~ 40 nm) of film in the annealed coating that is not observed in the as-deposited one. HRTEM image revealed that the top most layer is characterized by amorphous materials with embedded nanocrystalline particles.

The second mainstay of our research is study of photocatalystic TiO_2 films and TiO_2/Ge nanocomposite/nanolayered films for quantum dots (QDs) solar cell. In this field, HR-TEM/XPS are also necessary, which revealed that nanostructure of the TiO_2/Ge multilayered films. HR-TEM and XPS results clarified that interdiffusion between the Ge layer and the TiO_2 layer seems to be negligible, and metallic Ge is dominant in the 10 nm-thick Ge-layer with negligible Ge-oxide.

OPTICAL FLOATING ZONE METHOD CRYSTAL GROWTH AND NOVEL PROPERTIES OF RARE EARTH ORTHOFERRITES $RFeO_3$

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In recent years, rare-earth orthoferrites $RFeO_3$ (where R is a rare-earth ion) have attracted much interest in many applied and fundamental areas of condensed matter and materials physics, advanced materials and catalysis, mainly because of their novel physical properties such as magnetic, multiferroic, and superfast optomagnetic properties. Most of the devices require ideal single crystals, which have been grown using several techniques by many groups, but it is difficult to get high-quality single crystals. During the growth of high quality $RFeO_3$ single crystal, various problems were encountered in other technologies like hydrothermal method, Czochralski pulling, liquid-phase homoepitaxial method and the seeded Bridgman method. The optical floating-zone technique, with the advantages of being container free, non-polluting and possessing high growth rate, is the most effective method for the growth of $RFeO_3$ single crystal.

This talk will introduce the newly research progress on single crystal growth for the rare-earth orthoferrites $RFeO_3$ (R=Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er) by optical floating zone method, and show novel physical properties include spin reorientation transitions, low temperature multiferroics, ultrafast optomagnetic effects, anisotropic magnetocaloric effects, and spin precession motion excited by linearly polarized terahertz (THz) wave.

ZnO NANOWIRES WITH TiO_2 ADDITIVE AS ETHANOL NANOSENSORS

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ZnO nanowires with different TiO_2 additive (0-30 mol% TiO_2) were synthesized at 600-800°C for 12 h using a simple thermal oxidation reaction method under normal atmosphere. The characterizations of the nanowires were carried out and it was found that the highest numbers of the nanowires and the longest nanowires were observed at heating temperature of 600°C. The heating temperature was highly affected on number and size of the nanowires. The formation of the fcc-Zn_2TiO_4 phase was clearly observed from XRD and Raman results and higher fraction of the Zn_2TiO_4 phase was obtained as increasing heating temperature. The ZnO nanowires with different TiO_2 additive synthesized at 600°C were applied as the ethanol sensors and their ethanol sensing characteristics were investigated. The improvement of sensor response by TiO_2 additive was observed and can be explained by the reduction of electron concentration of sensor that caused by the formation of Zn_2TiO_4 phase. Thus, adding TiO_2 with ZnO nanowires is a promising technique for enhancement of sensor response.

STRUCTURAL AND OPTICAL PROPERTIES OF HEAT TREATED AND UV IRRADIATED CdS NANOPARTICLES

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CdS nanoparticles were synthesized by co-precipitation method using Cadmium acetate ($Cd(CH_3COO)_2$) and sodium sulfide (Na_2S) as ionic precursors. The samples were annealed in air for 3 h in steps of 100 °C in the temperature range of 200 –700°C to study the effect of both annealing temperature (T_a) on the structural and optical properties of CdS nanoparticles and UV photo-induced effect on the optical properties of the prepared nanoparticles. Structural and optical properties were investigated using X-ray diffraction (XRD), UV-Vis absorption spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The increase in the average crystallite size D from 2.67 to 23 nm as a result of annealing has been estimated from the broadening of X-ray diffraction lines. Substantial phase transitions at T_a = 300°C from as prepared Cubic CdS structure to CdS hexagonal structure and to $CdSO_3$ monoclinic structure at T_a = 700°C were discussed. Analysis of the UV-Vis optical absorption spectra refers to the validity of direct allowed transition with remarkable decrease in the direct band gap E_g^{opt} from 3.3 to 2.4 eV at 700°C with increasing T_a as a result of enhancement of crystallinity and increase in particle size which in turn leads to the reduction of quantum confinement effect. The observed phase transition and UV photo-induced changes were discussed in terms of the current models.

PREPARATION AND PROPERTIES OF $ZnO/AgO_x/ZnO$ TRANSPARENT CONDUCTING ELECTRODE ON FLEXIBLE PET SUBSTRATE

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Flexible organic solar cells have attracted a lot of attention due to their light weight, low cost, easy processing, and availability for large-scale production. The present work prepared a new type of transparent and conductive electrode $ZnO\text{-}AgO_x\text{-}ZnO$ (ZAOZ) film on a flexible PET substrate by magnetic control sputtering. Compared to the traditional electrode such as single-layer ITO or ZnO-Ag-ZnO (ZAZ), ZnO was applied as the oxide in OMO structure instead of ITO, and the micro-oxided AgO_x layer instead of pure Ag.

It was found that ZAOZ electrode was much more flexible than the traditional single-layer ITO electrodes. Since a better energy matching between ZnO and the photoactive polymer layer, the ZAOZ electrode was more suitable to construct the inverted organic solar cell. Due to the good electrical and optical performance of the electrode, the organic solar cell based on ZAOZ electrode exhibited much higher power conversion efficiency (6.34) compared to the organic solar cells based on ITO electrode (5.76) and ZAZ electrode (5.65%). What's more, the stability of the organic solar cell was improved a lot because of the inverted structure. The power conversion efficiency remained more than 85% of the initial value while the solar cell using conventional structure failed after 5 days.

ELECTROLYTES FOR IT-SOFC

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The aim of this work was to review solid electrolytes for the construction of intermediate-temperature solid oxide fuel cells, IT-SOFC. Yttrium stabilized tetragonal zirconia polycrystals, YTZP, have been highlighted as potential IT-SOFC electrolytes. Experimental results of my studies concerning structural, microstructural, electrical properties are presented in this work. The materials of YTZP were prepared using the co-precipitation method. The best microstructural and electrical properties from the viewpoint of application as solid electrolytes were observed for the samples modified by 0.5 mol% Al_2O_3 addition and sintered at 1500^oC. It was observed that the addition of alumina significantly improves grain boundary conductivity.

In order to study the diffusion of aluminium in 3YTZP, aluminium oxide was deposited on the surface of 3 mol% yttria stabilized tetragonal zirconia polycrystals (3Y-TZP). The samples were annealed at temperatures from 1523 to 1773 K. Diffusion profiles of Al in the form of mean concentration vs. depth in the B-type kinetic region were investigated by secondary ion mass spectroscopy (SIMS). Both the lattice (D_B) and grain boundary (D_{GB}) diffusion were determined.

Acknowledgements

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TUNING THE CRYSTALLOGRAPHIC STRUCTURE AND MORPHOLOGY OF NANOCRYSTALLINE CaB_6 FILMS DEPOSITED BY DC MAGNETRON SPUTTERING

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Through verifying the argon pressure, CaB_6 films with different crystallographic orientation and morphology on glass substrates were prepared by DC magnetron sputtering method. The film textures, crystallite sizes, composition and morphology were investigated using a spectrum of characterizing techniques in terms of X-ray diffraction (XRD), field emission scanning electron microscopy with energy dispersive spectrometer (SEM-EDS), atomic force microscopy (AFM), Raman shift spectroscopy. Influence of the argon pressure on the microstructure was studied. The average grain size increased with the argon pressure increased from 0.8Pa to 1.5Pa, meanwhile the dominant crystal face changed from (110) to (100). Then the grain size decreased when the argon pressure increased to 2.0Pa. The surface morphology evoluted from typically cauliflower-like nanocrystalline clusters to faceted rectangular pyramids. It's found that considerable amount of argon atoms were trapped in the films. The formation process of CaB_6 films was also analyzed in this paper.

ISO-CONVERSIONAL KINETIC STUDY OF NON-ISOTHERMAL CRYSTALLIZATION IN $Se_{89}In_6Pb_5$ CHALCOGENIDE GLASSES

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The crystallization kinetic of the $Se_{89}In_6Pb_5$ chalcogenide glass under non-isothermal condition using DTA technique is presented. Four iso-conversional methods (KAS–WFO–Tang–Starink) were used to calculate the local activation energy $E_c(\alpha)$. A small change of $E_c(\alpha)$ with the conversion (α) indicates a single step reaction mechanism. The calculated local Avrami exponent n(α) varies significantly with α from 3.5 to 1.0 which might be accounted for the change of crystallization character with conversion. The comparison between the experimental and calculated DTA curves based on the JMA model using constant and variable E_c and n at different heating rates is presented. The crystalline phases formed in the annealed samples were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

THE PROSPECTS IN DESIGNING NEW GENERATION OF HIGH TEMPERATURE COATINGS IN AUTOMOBILE ENGINES

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High temperature corrosion of outlet valves in automobile engines is still more and more important because of the presence of the aggressive combustion gases as well as increasing working temperature. Because of fundamental importance of this problem, extensive research is being made in order to minimize the corrosion of valve steels. The most important goal is to develop a new generation of high temperature inexpensive coatings, which could be used in automobile industry for protection of engine valves.

In this work, the oxidation behavior of new coatings under isothermal conditions in air has been studied, using microthermogravimetric technique. The application of thin chromium coatings for protection of valve steels increases the resistance of these steels against high temperature oxidation. This effect is a result of the formation of the scale built mainly from highly protective chromium oxide. The positive effect of chromium on the oxidation resistance of investigated steels is observed during much longer period of time than the life-time of the chromium coating, what strongly support the idea of tailoring of new generation of high temperature inexpensive coatings for automobile industry.

PLASMA ASSISTED CHEMICAL VAPOUR DEPOSITION – TECHNOLOGICAL DESIGN OF FUNCTIONAL COATINGS

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Plasma assisted chemical vapour deposition (PA CVD) is a wide used technology for the production of advanced materials and surface modification of different materials such as technical and medical titanium alloys, polymer surface, metallic substrates. This method allows to deposit of homogeneous, well-adhesive coatings at lower temperature on different substrates with complex shape. Plasmochemical treatment significantly impacts such surface parameters as microstructure, roughness, biological activity, hydrophobicity, free energy, mechanical and tribological behaviour, etc.

In this study we present the overview of the possibilities of PA CVD for the deposition of diamond-like carbon coatings, including doped Si and/or N atoms and modification of the polymer surface by plasma etching. Typical techniques for materials engineering such as scanning electron microscope (SEM) with EDS analysis, atomic force microscopy (AFM), X-ray diffraction, X-ray photoelectron spectroscopy (XPS), nanoindentation method (hardness and Young modulus), surface free energy and sessile drop technique were applied in the performer study.

Design of plasma technology, plasma surface functionalization and deposition of thin coatings on the titanium and aluminum alloy, PEEK substrate resulted in the hard and anti-wear structure with the improve of physicochemical parameters.

STUDY OF RUST PREVENTIVE CHARACTERISTICS OF RUST PREVENTIVE OIL FROM POLARIZATION CURVE MEASUREMENT

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Fe-Cu-C sintered steels are widely used. However, Cu, which acts as cathode enhance formation of rust (Fe_2O_3) during fabrication. To prevent formation of Fe_2O_3 rust preventive oils are generally used. High viscosity of those rust preventive oils decrease workability. While, low viscosity degrades rust preventive performance. Therefore, it is necessary to develop new rust preventive oils with contradictory properties of low viscosity and superior rust prevention. In this study, we developed technique to quantitatively evaluate rust prevention ability by measuring polarization curve through thin corrosive solution on Fe-Cu-C sintered steels coated with rust preventive oils. The electrochemical measurements were carried out corrosive solution of 0.35 mass % NaCl. Using a double capillary was added dropwise to the specimen. From the experiment, it is possible to evaluate the corrosion rate quantitatively in the surface of specimen, which was coated with rust preventive oil through thin corrosive solution. From the measurement results, corrosion rate is reduced by coating the rust preventive oil. Especially, corrosion rate, in case of coated with oil that the best performance showed 0.0001 times reduced in comparison without oil. Moreover, in case of coated with rust preventive oils the corrosion potential increased. Therefore, the anodic reaction is decreased with oils.

ENHANCEMENT OF PHASE SEPARATION AND ANISOTROPY SUPERCONDUCTIVITY IN Mn DOPED $K_{0.8}Fe_{2-y}Se_2$ SINGLE CRYSTALS

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Iron-selenides superconductors have attracted more attention since the discovery of T_c~30 K superconductivity in potassium intercalated $K_{0.8}Fe_{2-y}Se_2$ compound. In this work, we present the results of the transition metal Ni and Mn doping effects on the structure and superconductivity in $K_{0.8}Fe_{2-y}Se_2$ single crystals grown by self-flux method. For Ni doped samples, it was found that the random distribution of Ni on Fe or Fe-vacancy sites could suppress the superconductivity and induce spin disorders. And the slight Mn dopants could significantly enhance the phase separation of $K_{0.8}Fe_{2-x}Mn_xSe_2$ systems. For 3% Mn dopant, a second higher superconducting transition appears at $T_{c,onset}$=46.1 K and $T_{c,zero}$=32.6 K, which is the best result of intercalated iron-selenides superconductors so far. The origin of the enhancement effects was interpreted as the Mn dopants favorably distributes in iron vacancies ordered phase, which could well help the precipitations and modify the microstructure of superconducting phase by inducing the local lattice strain/distortion. Meanwhile, the improvement of sample quality allows us further study the anisotropic superconducting properties of the new superconducting phase with $T_{c,\ onset}$=46.1 K and $T_{c,\ zero}$=32.4 K in Mn doped $K_{0.8}Fe_{2-y}Se_2$ single crystal. Using Werthamer-Helfand-Hohenberg theory, the upper critical field $\mu_0 H_{c2}(0)$ at T=0 K for H//ab and H//c directions are estimated to be ~178.4 T and 52.6 T, respectively. A small anisotropic ratio Γ~3.4 is obtained. Due to its high upper critical field and low anisotropy, our results would stimulate further studies on the new superconducting phase.

PREPARATION OF TUNGSTEN OXIDE NANODOTS VIA THERMAL EVAPORATION METHOD AND THEIR APPLICATION TO NO_2 GAS SENSING

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WO_3 nanodots were synthesized by a developed and readily thermal evaporation method in ambient air. The size of the nanodots was about 8-12 nm. It was confirmed that the as-synthesized products have a WO_3 crystalline structure. The sensing ability of WO_3 dots-like structure configured as gas sensors was measured. The gas sensing measurements revealed that the nanoparticles in size of nanodots have numerous advantages in terms of reliability and high response. Due to its high surface-to-volume ratio and grain size less than Debye length, the sensor of nanodots of 8 nm in size exhibited the highest response. It is expected that this high response is due to the nanodots enters the region of volume depletion in air, exhibiting a dramatic improvement in response to NO_2 gas.

NANODOTS OF MULTIFERROIC PEROVSKITE $BiFeO_3$ FROM THE FIRST PRINCIPLES

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Multiferroic oxide nanodots might be harnessed to aid the development of the next generation of nonvolatile data storage and multi-functional devices. In this presentation, we introduce the computational aspects of multiferroic nanodot materials and designs that hold promise for the future memory technology. Conception, methodology, and systematical studies are discussed, followed by some up-to-date experimental progress towards the ultimate limits. At the end, we outline some challenges remaining in multiferroic materials research, and how the first principles based approach can be employed as an important tool providing critical information to understand the emergent phenomena in multiferroics.

Wei Ren, Advances in Manufacturing, 1, 166 (2013).

SELECTIVE EXCITATION AND POLARIZATION TRAJECTORY OF TERAHERTZ MAGNETIC DIPOLE RADIATION IN ORTHOFERRITE $PrFeO_3$ WITH IMPULSIVE POLARIZED TERAHERTZ RADIATION

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Single cycle terahertz (THz) pulses were employed to excite coherent spin waves in (110)-oriented $PrFeO_3$ single crystal. The free induction decay (FID) radiations at frequency of 0.34 THz (quasi-ferromagnetic mode, FM mode) and 0.41 THz (quasi-antiferromagnetic mode, AFM mode) were observed arising from the coupling of magnetic moment with the impulsive magnetic field of polarized terahertz radiation. These two spin modes in $PrFeO_3$ can be excited and modulated by the magnetic field of THz pulse with a specific polarization with respect to the crystal axis.

By using the polarized terahertz time-domain spectroscopy (THz-TDS), macro-magnetization motion in (110)-oriented $PrFeO_3$ single crystal was also constructed. We emphasize that trajectory of the emitted THz waveforms relies on not only the motion of macroscopic magnetization vector, but also the spin geometry and the propagation of THz pulse. The trajectories of electric field from the emitted FID signals for AFM mode are linearly polarized perpendicular to *c*-axis of $PrFeO_3$ crystal. For FM spin mode, as the incident THz pulse propagates perpendicular to the direction of M, the motion of M projected on the detection plane is observed as linear polarization, parallel to *c*-axis of crystal. The azimuthal angle (the incident THz pulse polarization with respect to crystal axes) enables us to control the polarization trajectories of the quasiferromagnetic (FM) and quasiantiferromagnetic (AFM) mode radiations, which can lead to further applications on multiple information storing and quantum processing.

TWOFOLD SPIN REORIENTATION AND FIELD INDUCED INCOMPLETE PHASE TRANSITION IN SINGLE-CRYSTAL $Dy_{0.5}Pr_{0.5}FeO_3$

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Rare earth orthoferrites ($RFeO_3$) have a distorted perovskite structure. For some orthoferrites, the net magnetization rotates by 90^o as the temperature varies between characteristic temperatures. This phenomenon, referred to as spin reorientation (SR), has been studied in different orthoferrites, and is being greatly revived because this transition is closely related to the magnetically driven ferroelectricity. Here, we focus our investigation on the M-T under different applied fields and M-H below the SR transition temperature T_{SR1} ~ 77 K for $Dy_{0.5}Pr_{0.5}FeO_3$ single crystal. The results show some remarkable phenomena: (1) twofold spin reorientation transitions of type $\Gamma_4 \rightarrow \Gamma_1 \rightarrow \Gamma_2$ for the Fe^{3+} magnetic sublattice at SR temperature T_{SR1} ~ 77 K and T_{SR2} ~46 K. In particular, the sharp transition of type $\Gamma_4 \rightarrow \Gamma_1$ from $\mathbf{77\ K}$ to 76 K implies that $Dy_{0.5}Pr_{0.5}FeO_3$ single crystal may find potential use for temperature induced fast magnetic-switching devices like that may be used for liquid nitrogen level gauge; (2) An obvious field-induced incomplete spin transition ($\Gamma_4 \rightarrow \Gamma_{41} \rightarrow \Gamma_{42}$ for H = 10 kOe and $\Gamma_4 \rightarrow \Gamma_{42}$ for H = 40 kOe) was observed (3) $\mathbf{T_{SR}}$ of $Dy_{0.5}Pr_{0.5}FeO_3$ single crystal can be controlled by changing the magnitude of applied magnetic field; (4) Spin reorientation of type $\mathbf{\Gamma_1 \rightarrow \Gamma_4}$ is induced by a sufficiently larger magnetic field along $\boldsymbol{c}$ axis. By comparing with the M-H at different temperatures, we monitor the relative change of critical field H_{cr}. It is this instability that generates the intriguing phenomena such as incomplete SR and magnetic field-induced SR.

DOPING CONTROLLED SPIN REORIENTATION IN DYSPROSIUM-SAMARIUM ORTHOFERRITE SINGLE CRYSTALS

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As one of the most important phase transitions, spin reorientation (SR) draws much attention of emerging technologies. The origin of SR is the competition between different spin configurations which possess different free energy. There are two different SR types with respect to different initial spin configurations of RFeO$_3$: Γ_2 to Γ_4 and Γ_1 to Γ_4. It is interesting whether the type of SR will take place in orthoferrites which possess two different SR type rare earth ions. To focus on the control of SR, we introduce a single crystal family $Dy_{1-x}Sm_xFeO_3$ (DSFO), which were grown by an optical-floating-zone method and characterized by various technics, to this study. Three remarkable phenomena were found in the measurements: (1) there is a linear change of SR transition temperature of both Dy-rich for $x<0.2$ and Sm-rich samples for $x>0.2$; (2) jumps appear at <50 K temperature region in a-axis magnetization FCC process curves of the single crystal $Dy_{1-x}Sm_xFeO_3$ ($x=0.5$-0.9); (3) a- and c-axis magnetization of the crystals indicate that Dy concentration in Sm-rich samples will change the antiparallel coupling between Sm sublattice moment and Fe sublattice net moment to parallel coupling. The linear control of SR transition and special magnetic behavior will be serviceable in spintronics application.

MAGNETIZATION SWITCHINGS OF RARE EARTH ORTHOCHROMITE $CeCrO_3$

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Rare earth orthochromites $RCrO_3$ perovskites have attracted considerable interest for their complex magnetic phases at low temperature in the past, and more recently for their potential magnetoelectric or multiferroic properties. Among all rare earth-based perovskites, Ce^{3+}-based ones (such as $CeCrO_3$, $CeFeO_3$) are scantily reported, as Ce^{3+} is prone to oxidation, which leads to phase separation of the ABO_3 structure. Shukla et al. reported the preparation and properties of nanocrystalline $CeCrO_3$. However, more detailed data about its physical properties of the bulk $CeCrO_3$ are desirable. In this work, we report the synthesis of single phase polycrystalline $CeCrO_3$, and the magnetic properties in such rare earth perovskite chromite by varying temperature and magnetic field. We have found a canted antiferromagnetic transition with thermal hysteresis at T=260 K, indicating a first-order phase transition. Moreover, a magnetic compensation (zero magnetization) near 133 K is attributed to the antiparallel coupling between Ce^{3+} and Cr^{3+} moments. At low temperature, field induced magnetization reversal starting from 43 K for H=1.2 kOe reveals the spin flip driven by Zeeman energy between the net moments and the applied field. These findings may find potential uses in magnetic data storage and switching devices such as nonvolatile magnetic memory which facilitates two distinct states of magnetization.

ELECTRON MICROSCOPY OF CARBIDES IN HIGH CHROMIUM CAST IRONS WITH 0-10wt% ADDITION OF MOLYBDENUM OR TUNGSTEN

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High chromium cast irons with 28wt%Cr are of interest due to their promising wet wear performance. Mo and W are carbide-forming elements which have been added to modify the microstructure of these irons to improve their abrasion wear performance, however carbide identification in these irons as reported in literatures is not in full agreement. In the present work, electron microscopy of carbides in 28wt%Cr cast irons, with the Cr/C ratio of about 10 and addition of Mo or W up to 10wt%, was therefore carried out. It was found that addition of Mo or W promotes formation of $M_{23}C_6$ and M_6C, instead of the typical M_7C_3 well-defined in the iron without Mo or W addition. Distinctive characteristics of M_7C_3, $M_{23}C_6$ and M_6C found in these irons will be addressed, based mainly on results from energy dispersive X-ray spectroscopy. A carbide transition as $M_7C_3(M_{2.3}C)$->$M_{23}C_6(M_{3.8}C)$->M_6C was indicated in these irons. Generally, Si content and relatively high Mo content are important characteristics of M_6C, whereas $M_{23}C_6$ has higher Fe/Cr and Mo/Cr atm.% ratios than those in M_7C_3.

SOLUTE-VACANCY CLUSTERING IN Al-Mg-Si ALLOYS STUDIED BY MUON SPIN RELAXATION TECHNIQUE

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High energy-efficiency is a common requirement in industries, in which Al-Mg-Si alloys are in high demand as a material for vehicles because of their low weight, excellent formability and age-hardenability. A key factor has been considered to be vacancy behavior which stimulates diffusion of Mg and Si, and forming clusters. We have commenced muon spin relaxation spectroscopy to study the behavior of vacancies in Al-Mg-Si alloys. The recovering tails of the observed muon spin relaxation functions give us rich information on muon hopping between vacancies and other defects in Al alloys. Our recent work with Al-1.6%Mg2Si, Al-0.5%Mg, and Al-0.5%Si alloys has demonstrated that the muon trapping rates (*nt*) depend on the heat treatment and solute concentrations: 1) the concentration of dissolved Mg dominates the *nt* at lower temperatures below 120 K, 2) the *nt* around 200 K reflect a number of clusters and vacancies, 3) a natural aging effect is observed only with Al-0.5%Si. This contribution will review our recent results of muon spin relaxation versus temperature, and will give detailed discussions about the effect of the heat treatments on the *nt*. An attempt will be made to estimate the binding energies of Mg-muon and vacancy-muon by using Arrhenius plots.

ROLE OF BACK-SCATTERED ELECTRONS IN THE SCANNING ELECTRON MICROSCOPE AT LOW PRIMARY ELECTRON ENERGIES

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Signal of Back-Scattered Electrons (BSEs) is one of the most often used signals for the imaging of materials in the Scanning Electron Microscope (SEM). We studied the angular distribution of the BSEs emitted from the specimen using the multichannel detector. This was performed at various energies of the primary electrons (PE). The optimum primary beam energy from the point of view of crystallographic contrast was found to be around 500 eV. The crystallographic orientation of the grains can be determined also from the measurement of the reflectivity of BSE signal as a function of the PE beam energy, below 50 eV. The advantage of this method is higher lateral resolution in comparison to the conventional EBSD method. A special aberration corrector for the objective lens was designed in order to decrease the spot size, which was obtained as follows: 0.6 nm at 2 keV PE energy, 0.8 nm at 200 eV and 4,5 nm at 20 eV. Both methods can be very useful for the study of modern materials formed by small crystals, which is impossible by a standard EBSD. The use of the angle-sensitive detector can be useful even for the imaging of less conductive, uncoated materials. The emitted signal electrons which are responsible for the charging can be separated by controlling the distribution of the electrostatic and magnetic fields in the specimen region, thereby influencing their trajectories.

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DENSITY FUNCTIONAL THEORY STUDY OF THE INTERACTION OF HYDROXYL GROUPS WITH IRON SURFACE

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In the elementary process of the aqueous corrosion on the surface of iron, the role of water and oxygen molecules on the surface is important. Hydroxyl (OH) groups could appear on the iron surface due to the dissociation of water molecules. Periodic density functional theory (DFT) calculations were used to study the interaction of OH groups with iron surface from atomic scale computations. The iron surface was represented by five layers, with the calculated lattice constant (a=2.882 Å) of BCC structure and a vacuum region of 20 Å. The bottom layer was fixed in the bulk lattice positions and all other atoms were allowed to relax until the forces on unconstrained atoms converged to less than 0.01 eV/Å. The calculated result of the binding energy demonstrated that the interaction on OH groups and the surface of iron is strong. It is likely to be due to the interaction of the lone-pair electrons of oxygen and the 3d orbital electrons of iron atom. Our calculations show that OH is most stable in the bridge site, and that the orientation of the O-H bond is tilted at a 69 degree angle to the surface normal. We also found that the binding energy is decreasing with the increase of surface coverage.

STRUCTURE AND BIOMECHANICS OF *COMMON REED* CANES USED FOR JAPANESE DOUBLE REED WIND INSTRUMENT "*HICHIRIKI*"

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Hichiriki is a traditional Japanese double-reed wind instrument used in Japanese *gagaku*, ancient imperial court music, since the 7th century. Reeds are thin pieces of cane inserted into the tube of certain wind instruments such as clarinet, oboe, bassoon and hichiriki, to set in vibration the air column inside the tubes. For more than 1200 years, the best reeds for the hichiriki have been made only out of canes of *common reed* (*Phragmites australis*) that are harvested from 'Udono' which is a limited reed bed of riverbanks near Kyoto along the Yodo River. Here, we elucidate why the canes from Udono are the best materials for *hichiriki* reeds. We examined the plant anatomical structure of *common reed* canes grown in different reed beds in Japan, and performed the local indentation hardness and Young's modulus measurements of tissues on cross-sections of different *hichiriki* reeds. It is revealed that good canes for *hichiriki* reeds have an outer diameter of about 11 mm, a wall thickness of about 1 mm and comparatively homogeneous structure, where harder materials such as epidermis, hypodermis, sclerenchymatous cells and vascular bundle sheaths are orderly deployed with softer materials such as parenchyma cells and vascular bundles. This structure has smaller differences in hardness and Young modulus between the hard and soft materials in the *hichiriki* reed, providing the best music performance.

The authors deeply thank Ms. Hitomi Nakamura, the *Reigakusha Gagaku Ensemble*, for providing the samples of *common reed* canes and hichiriki reeds, with valuable comments from a view of musical performance. The light microscopy observation was performed using facilities at Laboratory of Forest Utilization, Graduate School of Agriculture, Kyoto University.

FABRICATION OF CeO_2-TiO_2 COMPOSITED THIN FILMS ON GLASS SUBSTRATE FROM AQUEOUS SOLUTION BY ELECTRO-CHEMICAL DEPOSITION METHOD AND THEIR OPTICAL PROPERTY

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In this study CeO_2 precursor thin films with TiO_2 particles were deposited onto ITO/glass substrates at a room temperature from an aqueous solution by applying constant electrical field and their optical properties were investigated. The precursor was an aqueous solution of $Ce(NO_3)_3$-$6H_2O$, $M(NO_3)_3$-$6H_2O$ (M:Gd,Sm.Y), NH_3(aq) and the TiO_2 powder. The thin film was deposited on the ITO/glass substrate of the minus electrode. By applying the electrical field of 2.0-3.0 V, the $Ce(OH)_3$ thin film was effectively deposited with TiO_2 particles on glass substrates at room temperature. The as-deposited film was amorphous, and a crystalline phase of CeO_2 can be obtained after annealing at 823 K for 5 h in air. Spectral transmission curves of visible to ultraviolet light region through CeO_2-TiO_2 composited thin films were measured and about 10 to 30 % absorption peaks were observed around 310 and 420 nm. The relation between growth conditions, surface morphology and their interceptor properties of ultraviolet light region were studied.

MAGNETIC AND ELECTRONIC PROPERTIES OF CAGE-STRUCTURED COMPOUNDS RTi_2Al_{20} (*R*: HEAVY RARE EARTHS)

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Recently, cage-structured compounds such as filled skutterudites have attracted much attention due to the novel properties such as the heavy fermion behavior and the first observation of unconventional superconductivity in the Pr-based filled skutterudites, and multiple ordering. These novel properties are coming from the low-lying crystal electric field (CEF) due to the crystal structure. Among them, the compounds RT_2Al_{20} (*R*: rare earth, *T*: transition metal) also have the caged and cubic structure. These compounds also show the novel properties. However, only a few compounds (*R* = Pr, Sm) are studied. To clarify these novel properties, systematic studies are important. Recently, we were succeeded in making new RTi_2Al_{20} (*R*: heavy rare earths), and studied magnetic and electronic properties.

RTi_2Al_{20} were made by the arc melting method. The obtained sample were measured by the Powder X-ray diffraction analysis. Most of the observed diffraction lines are indexable using $CeCr_2Al_{20}$ type structure and lattice parameters are determined.

The temperature dependences of the resistivity (ρ) for RTi_2Al_{20} (*R* = Gd, Tb,and Dy) show the metallic behaviors at ~ 300 K. With decreasing temperature, ρ decreases and show weak shoulder ~ 150 K. For $TbTi_2Al_{20}$, $DyTi_2Al_{20}$, and $HoTi_2Al_{20}$, ρ also shows the shoulder ~ 30 K. The residual resistivity ratio (RRR) becomes ~ 16 at maximum value, suggests the high quality of the sample.

DENSITY FUNCTIONAL THEORY CALCULATIONS OF HYDROGEN DIFFUSION IN ALUMINUM

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For hydrogen diffusion of the metal, an understanding of the interaction of hydrogen and vacancy is a fundamental problem, and it is also very important. Recently, density functional theory (DFT) calculations have become a complement to experimental approaches for studying the diffusion of hydrogen in metals and other solids. Hydrogen atoms dissolve into bulk aluminum, where they can reside in either the octahedral or tetrahedral interstitial sites. Hydrogen is able to diffuse through the octahedral and tetrahedral site. In order to investigate the influence of vacancy and substitutional atoms (Mg, Si) for H diffusion in Al, the study was performed using DFT calculations. We used a supercell with 32 Al atoms in a simple cubic lattice as model bulk Al. The Generalized gradient approximation (GGA) was used in all of our calculations, with checks based on the local density approximation (LDA). Our calculations included a nudged elastic band (NEB) calculation of the diffusion paths and the diffusion barriers. The NEB calculation results on H diffusion demonstrated that the activation energy of the case with vacancy is 0.546 eV. This result shows that the interaction of hydrogen atoms and vacancies is strong. This is consistent with previous studies using DFT calculations. The hydrogen diffusion path in the case of a substitutional atom Si was also found to be different from the others.

CRYSTALLIZATION KINETICS OF OVERLAPPING PHASES IN $Se_{70}Te_{15}Sb_{15}$ USING ISOCONVERSIONAL METHODS

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Differential Scanning Calorimetry (DSC) under non-isothermal conditions has been used to study the crystallization of $Se_{70}Te_{15}Sb_{15}$ chalcogenide glass. This glass was found to have a double glass transition and double overlapped crystalline phases. The overlapped crystalline phases were separated successfully using Gaussian fit model. The activation energy, E_c, and Avrami index, n, were determined by analyzing the data using the Matausita et. al. method. A strong heating rate dependence of the activation energy for the two crystalline phases was observed. The variation indicates that the transformation from amorphous to crystalline phases is a complex process involving different mechanisms of nucleation and growth. The varition of activation energy with crystalline fraction was determined by Kissenger- Akahira-Sunose (KAS) method. Results obtained directly by fitting the experimental DSC data to the calculated DSC curves indicate that the crystallization process of $Se_{70}Te_{15}Sb_{15}$ glass cannot be satisfactorily described by the Johnson-Mehl-Avrami (JMA) model. Simulation results indicate that the Sestak-Berggren (SB) model is more suitable to describe the crystallization process for the studied glass. Reasons of the deviations from JMA model were also discussed. On the other hand, the crystalline phases for the events were identified using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

ANODIC ALUMINUM OXIDE AS MATRIX FOR Li-COMPOSITE ELECTROLYTE

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The study of porous alumina structures has attracted the attention of the scientific community because of their interesting features, which can be leverged for energy storage and many other applications of nanotechnology [1-2]. To fabricate porous anodic alumina, one uses electrochemical etching (anodization) of aluminum in acidic electrolyte. Most anodization procedures that generate straight pores are done at temperatures below 5˚C in sulfuric, oxalic and/or phospheric acids, as reported in the literature [3]. However in this work, we introduce a novel, simple one-pot synthesis method to develop thin walls of aluminum oxide that conatian lithium ions, for Li-ion battery applications. The anodization of Al films was conducted in a supersaturated mixture of lithium phosphate and 0.75 M phosphoric acid, as a matrix for the Li-composite electrolyte. For this purpose, aluminum films, a few micrometers thick, were fabricated. Our results show that both the anodization rate and current density, in the transient curve, decreased as the concentration of LiH_2PO_4 in H_3PO_4 increased. Moreover, the wall thickness becomes thinner for samples anodized in higher concentration of LiH_2PO_4 in H_3PO_4.

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STRUCTURAL, MORPHOLOGICAL AND OPTICAL CHARACTERIZATIONS OF ANNEALED EDTA CAPPED ZnS NANOCRYSTALS PREPARED BY CHEMICAL PRECIPITATION METHOD

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ZnS nanocrystals were prepared by chemical co-precipitation method using zinc acetate ($Zn(CH_3COO)_2$) and sodium sulfide (Na_2S) as ionic precursors and EDTA as a capping agent. The samples were annealed in air for 3 h in steps of 100 °C in the temperature range of 125–700 °C. The effect of annealing temperature (T_a) on the morphological structural and optical properties of ZnS nanoparticles was investigated using X-ray diffraction (XRD), High resolution transmission electron microscope (HRTEM), Optical absorption spectroscopy (OAS), selected area electron diffraction (SAED) and Fourier transform infrared (FTIR) spectroscopy. Analysis of XRD patterns for as prepared and annealed samples using scherrer equation showed that increasing in (T_a) leads to an increase in the crystallite size (D) from 2.67 to 20 nm. It is found large discrepancy between the mean values of the particle size calculated from XRD pattern and that obtained from TEM images. In addition, it is noticed that the obtained values of lattice parameters from (HRTEM) and (SAED) pattern are in a good agreement with that deduced from (XRD) analysis. Furthermore, annealing process at 600 ^oC and 700 ^oC results in completely phase transformation from as prepared ZnS cubic Structure (ZB) to ZnO hexagonal structure (WZ). Analysis of the XRD patterns and FTIR spectra confirmed this phase transition. Moreover, analysis of the optical absorption spectra according to Tauc's equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ for direct allowed optical transition indicates remarkable decrease in the direct band gap E_g^{opt} from 4.1 to 2 eV with increasing T_a. This behavior is due to an increase in the degree of crystallinity as shown from (XRD) analysis and an increasing the particle size of ZnS nanoparticles as observed in TEM images and (SAED).

MODEL RESEARCH ON SYNTHESIS OF Al_2O_3-C LAYERS BY MOCVD

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These are model studies whose aim is to obtain information that would allow to develop new technology for synthesis monolayers of Al_2O_3-C with adjusted microstructure on cemented carbides. Al_2O_3-C layer will constitute an intermediate layer on which is synthesized the outer layer of Al_2O_3 without carbon. The purpose of the intermediate layer is to block the cobalt diffusion to synthesized outer layer of Al_2O_3 and stopping the diffusion of air oxygen to the substrate during the synthesis of the outer layer. This layer should be thin, continue, dense and uniform in thickness. For this purpose, a transparent quartz glass is used, which allows a quick visual assessment of the layers, their thickness and distribution as well as allows to determine whether the process of homogeneous nucleation occurred. This process results in hazy layers as a result of the formation the porous powders in gas phase. Al_2O_3-C layers were synthesized of aluminum acetylacetonate by CVD method on quartz glass heated in an induction furnace in the temperature range 800 -1000°C using argon as a carrier for the reactants. The resulting Al_2O_3 layer contains carbon, which caused dark colored layers. Dark-colored layers show that the carbon exists in the form of clusters not of individual atoms, in which in addition to σ bonds there are π bond. The layers were prepared also at low temperatures and next were subjected to crystallization at higher temperatures. The resulting layers prepared at temperatures above 900°C were nanocrystalline (included phase α-Al_2O_3).

MODEL RESEARCH ON DEPOSITION OF PURE ALUMINIUM OXIDE LAYERS BY MOCVD METHOD

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The purpose of this research is to develop an optimal method for synthesis of nanocrystalline monolayers Al_2O_3 structure suitable for application of high speed growth on cemented carbides coated with an intermediate layer of pre-Al_2O_3-C (composite layers Al_2O_3-C/Al_2O_3). The use of quartz glass substrate, because of its high transparency, allows to get information about the quality of the layers such the thickness and density. Homogeneous nucleation process can have a significant effect on the density of the deposited layers. This process leads to the formation of porous powders, which are embedded on the synthesized layer (their composition is similar or the same as the synthesized layer). Then, the resulting layer is visually opaque. These layers are, characterized by high porosity and poor adhesion to the substrate. It should be noted that the use of the expression in the study developed Gr_x/Re_x^2 (Gr-Grashof number, Re-Reynolds number, x-distance from the gas inflow point; values of gas parameters at this distance are subscripted x) also allows to quickly determine the appropriate process parameters. The Al_2O_3 layers on quartz glass, not containing carbon were synthesized by MOCVD using aluminum acetylacetonate and air as the reactant at temperatures of 700-1000^{o}C. Argon was a carrier gas. The resulting layers were transparent, as in the process of their synthesis homogeneous nucleation did not occur. The layers synthesized at lower temperatures were subjected to a crystallization process at temperatures above 900^{o}C. Crystallization process was studied in function of time and temperature. Resulting layers were characterized by their nanocrystalline structure.

GAS SENSING APPLICATIONS OF TiO_2 BASED NANOMATERIALS

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The aim of this research is to examine gas sensing applications of TiO_2 based nanomaterials. TiO_2 nanostructures modified by doping and controllable changes in the grain size were obtained by Flame Spray Synthesis, FSS, technique. Nanomaterials were characterized by standard techniques available, namely optical spectrometry UV – vis with the use of an integrating sphere, X – ray diffraction, XRD, Brunauer – Emmett – Teller adsorption isotherms, BET, Scanning Electron Microscopy, SEM and Transmission Electron Microscopy, TEM, as well as impedance spectroscopy. Detection of hydrogen was carried out over the concentration range of 50 - 3000 ppm at the temperatures extending from 200 to 400 ^oC and synthetic air working as a reference atmosphere. The sensor response was defined as: $S = (R_0-R)/R_0$ where R_0 denotes electrical resistance in the reference atmosphere and R is its value upon interaction with H_2.

As a result of experiments it appears that well – crystallized, spherically shaped TiO_2 based nanostructures can be successfully used for hydrogen sensing applications.

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PRECIPITATION IN Al–Cu–Mg(–Zn) ALLOYS

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The alloy systems Al–Cu–Mg (2*xxx*) and Al–Zn–Mg (7*xxx*) are hardened by metastable nano-precipitates formed during heat treatment. The precipitate phases of the two systems are very different: 2*xxx* alloys have GPB-zones and S phases, which are needle-shaped, and have their main growth and coherency directions along $<001>_{Al}$. In 7*xxx* alloys, the equilibrium η phase and its precursors grow mainly as plates parallel to $\{111\}_{Al}$ planes. In a context of formation enthalpy of the precipitates and diffusion of the different solute elements, it is interesting to find out if the two situations can coexist in the same material. To address this, we have investigated the evolution of hardness, conductivity and presence of the relevant precipitate types during artificial ageing of Al–Cu–Mg(–Zn) alloys. Transmission electron microscopy was used for determining the precipitate microstructure in under- and over-aged conditions.

Nb-O-N THIN FILMS DEPOSITED BY LOW VACUUM REACTIVE SPUTTERING

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Nb-O-N film deposited by sputtering is investigated as photo-semiconductor material. They have been researched as high-efficiency solar panel, because the niobium oxy-nitride film is reported to absorb light of longer wave length compared to the existing solar panel materials. In this study, we attempted to observe the composition change by changing nitrogen gas flow ratio in sputtering. The soda glass substrate and (100) silicon wafer was used as substrate. The 99.95% purity niobium target was used. The base pressure was 2.5 Pa. Argon and nitrogen gas purity were six-nine grades. Nitrogen gas flow rate was varied for change the films composition. For the film deposited in 4% nitrogen gas ratio, the film had like bcc-$NbN_{0.9}O_{0.1}$ structure by XRD. Lattice spacing along the film surface were larger than the value of the card date.

ION-EXCHANGE REACTION OF A-SITE IN $A_2Ta_2O_6$ PYROCHLORE CRYSTAL STRUCTURE

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Na^+ or K^+ ion rechargeable battery has started to garner attention recently in place of Li^+ ion cell. It is important that A^+ site ion can move in and out the positive-electrode materials. When $K_2Ta_2O_6$ powder had a pyrochlore structure was only dipped into NaOH aqueous solution at room temperature, $Na_2Ta_2O_6$ was obtained. $K_2Ta_2O_6$ was fabricated from a tantalum sheet by a hydrothermal synthesize with KOH aqueous solution. When $Na_2Ta_2O_6$ was dipped into KOH aqueous solution, $K_2Ta_2O_6$ was obtained again. If $KTaO_3$ had a perovskite structure was dipped, Ion-exchange was not observed by XRD. Because a lattice constant of pyrochlore structure of K-Ta-O system is bigger than perovskite, K^+ or Na^+ ion could shinny through and exchange between Ta^{5+} and O^{2-} ion site in a pyrochlore structure. K+ or Na+ ion exchange of $A_2Ta_2O_6$ pyrochlore had reversibility. Therefore, $A_2Ta_2O_6$ had a pyrochlore structure can be expected such as Na^+ ion rechargeable battery element.

EFFECT OF DEMOLD PROCESS ON SOLIDIFICATION STRUCTURE OF Mg-9%Al-0.3%Mn SYSTEM ALLOY

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Mg-Al system alloys have the characteristic with high specific tensile strength and lightweight properties, and it is applied to automobile and transportation components produced by mainly High-pressure die-cast method (HPDC) in recent years. However mechanical properties were not superior, because of existing of the non-equilibrium crystallized phase and coarse precipitate. In this study, we investigated the effect of the cooling process on the solidification structure after casting, in order to improve the mechanical properties in Mg-9%Al-0.3%Mn alloy. As a result, in the case of holding temperature was relatively higher at 673K after cooling down from as-cast state, the value of volume fraction of non-equilibrium crystallized phase was decreased with the holding time increased due to solid solution in the matrix. On the other hand, holding temperature was relatively lower at 473K, the precipitated phase was increased with the holding time increased. Therefore, it is suggested by cooling and holding method after as-solidified can be controlled.

INVESTIGATION OF DISCONTINUOUS PRECIPITATION BEHAVIOR IN Mg-9%Al-0.3%Mn ALLOY CAST BY SAND MOLD

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[3]Hokuriku Polytechnic College;
[4]Ahresty Corporation

Mg-Al system alloy has the characteristic with high specific tensile strength and lightweight property, it is used for automotive components. The precipitate reactions of Mg-Al alloy are distinguished discontinuous and continuous precipitation. Discontinuous precipitation is occurred preferential precipitation during the early stage of aging. On the other hand, continuous precipitation is usually occurred after the discontinuous precipitation. Both precipitate reactions are competitive, therefore these behavior are strengthly affect to properties in Mg-Al alloy. However, there are few reports about discontinuous precipitation behavior of Mg-Al alloy. In this study, discontinuous precipitation behavior after solutionization and artificial aging process of Mg-9%Al-0.3%Mn alloy cast by sand mold is investigated by activation energy calculated from volume fraction of discontinuous precipitation. Result of this study, measured activation energy of the alloy is 78.3kJ/mol, it is similar to value of grain boundary diffusion reported in the past studies. Therefore, it is estimated grain boundary diffusion is dominant in Mg-9%Al-0.3%Mn alloy.

EFFECT OF Al AND Mn CONTENTS ON PRECIPITATION BEHAVIOR OF Mg-Al-Mn ALLOY

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Magnesium alloy is the lightest of all conventional alloys used in industrial field. Especially, Mg-Al-Mn alloys are widely used in automotive components due to their good strength and ductility. In this study, influence of Al and Mn content on the aging behavior of Mg-4-7mass%-0-0.6mass%Mn alloy was investigated. All alloys were cast into Y-block shaped metal molds and then aged after solution treatment at 688K for 86.4ks. We found that only discontinuous precipitation was observed in microstructures of Mg-4mass%Al alloy aged at 473K for 1382.4ks. However, Al content higher than 6mass% alloys aged at 473K for 21.6ks, continuous and discontinuous precipitation were observed clearly in microstructures. The amount of both precipitations increased with increasing aluminum content of the alloys. There was no remarkable difference in the aging behavior and microstructures with increasing Mn content from 0mass% to 0.6mass% on Mg-7mass%Al.

STUDIES ON AN AEROBIC OXIDATION OF DIBENZOTHIOPHENE AND RELATED COMPOUNDS USING RUTHENIUM CATALYST

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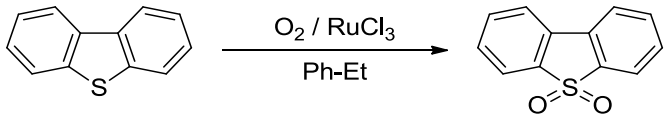
From an increase of environmental concern, special interests had been paid for reduction of organosulfur compounds in transportation fuels. Under these situations, oxidative desulfurization (ODS) was proposed in 1990s. Oxidation reactions of sulfur compounds are involved as a key step of the ODS process. Therefore, many papers concerning oxidation of sulfides have been published. In this study, the authors had found that dibenzothiophene (DBT) and related compounds could be oxidized to the corresponding sulfones by molecular oxygen in the presence of a ruthenium catalyst in hydrocarbon solvents under relatively mild conditions. These results will be reported briefly.



A mixture of DBT and ruthenium(III) chloride in ethylbenzene (EB) was stirred at 80 °C for 20 h under molecular oxygen. After the reaction, a product mixture was analyzed by a gas chromatograph, indicating that DBT was consumed completely and dibenzothiophene-5,5-oxide (sulfone) was produced in an almost quantitative yield. Other oxidized products from DBT such as sulfoxide were not detected by GC analysis. At 70 °C, conversion of DBT was rather low.

Acetophenone, 1-phenylethanol, and 1-phenylethyl hydroperoxide were also observed as by-products derived from EB. Based on these results, the present reaction of DBT might proceed *via* the following two steps: The first step is autoxidation of EB to the hydroperoxide and the next step is oxidation of DBT to the sulfone by the hydroperoxide produced. The authors also investigated the effects of solvents, and catalysts on the reaction efficiency.

FABRICATION OF YSZ THIN FILM BY ELECTROCHEMICAL DEPOSITION METHOD AND THE EFFECT OF THE PULSED ELECTRICAL FIELDS FOR MORPHOLOGY CONTROL

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In this study, surface morphology control and patterning has been carried out during deposition of thin film from a precursor solution by applying the electrical field for deposition and the pulsed electrical field at the same time. The precursor solution was mixed $ZrO(NO_3)_4$, $Y(NO_3)_3$ $-6H_2O$ into deionized water, and then was controlled nearly pH=3 by adding NH_3(aq). The thin film was deposited on the glass substrate of the minus electrode side. By applying the electrical field of 3.0 V, the $Zr(OH)_4$, $Y(OH)_3$ thin film was effectively deposited on glass substrates at room temperature. The as-deposited film was amorphous, and a crystalline phase of YSZ could be obtained after the annealing at 773 K for 6 h in air. In order to establish to morphology control and patterning, another pulsed voltage was applied to the electrical field along the perdicular direction to the film deposition direction. In the limited condition, the striped patterns of YSZ films due to the frequency of the applied electrical field were observed.

SYNTHESIS OF Fe DOPED $LiMn_2O_4$ CATHODE MATERIALS FOR Li BATTERY BY SOLID STATE REACTION

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$LiFe_{0.1}Mn_{1.9}O_4$ is expected as a cathode material for a rechargeable lithium-ion batteries. $LiMn_2O_4$ has received attention because this has advantages such as low cost and low toxicity compared with other cathode materials such as $LiCoO_2$ and $LiNiO_2$. However, $LiMn_2O_4$ has some problems such as low capacity and low life. $LiMn_2O_4$ has phase transformation at around room temperature. One of the method to overcome this problem is to stabilize the spinel structure by substituting Mn in $LiMn_2O_4$ with transition metals (Al, Mg, Ti, Ni, Fe, etc.). $LiFe_{0.1}Mn_{1.9}O_4$ spinel was synthesized from Li_2CO_3, Fe_2O_3 and MnO_2 powder. The purpose of this study is to report the optimal condition of Fe doped $LiFe_{0.1}Mn_{1.9}O_4$. Li_2CO_3, Fe_2O_3, and MnO_2 mixture powder was heated up to 1173 K by TG-DTA. Li_2CO_3 was thermal decomposed, and CO_2 gas evolved, and formed Li_2O at about 800 K. $LiFe_{0.1}Mn_{1.9}O_4$ was synthesized from a consecutive reaction Li_2O, Fe_2O_3 and MnO_2 at 723 ~1023 K. Active energy is calculated to 178 $kJmol^{-1}$ at 723 ~ 1023 K. The X-ray diffraction pattern of the $LiFe_{0.1}Mn_{1.9}O_4$ heated mixture powder at 1023 K for 32 h in air flow was observed.

EFFECTS OF ALUMINUM SPUTTERING ON THE CORROSION RESISTANCE OF AZ91 ALLOY

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Magnesium alloys, which are lightest among the practical metals, have dimensional stability and electromagnetic shielding. These properties have been applied in many fields. However, the corrosion resistance is low, owing to its electrochemical property. Therefore, we examined aluminum deposition, which was made by sputtering on AZ91 magnesium alloy's surface, aiming to prove corrosion resistance for it. Corrosion resistance of the aluminum deposited AZ91 was evaluated by electrochemical methods, in which corrosion rates were obtained by Tafel extrapolation method of polarization curves. Observation of surface cross-section and chemical compositions analysis of tested pieces were conducted by SEM-EDS. The formation of aluminum deposition on AZ91 could not improve the corrosion resistance due to the deposition defects. Then, after aluminum deposition, conduced heat treatments at 553K, 623K, 673K for 3 hours in an Ar atmosphere, respectively. These specimens were analyzed by the same test. It was recognized that the diffusion layer formed between the substrate and the aluminum deposition in the heat treatment at 553K for 3 hours. The diffusion layer improve the corrosion resistance. However, in the cases of heat treatment at 623 K and 673 K, the corrosion resistance was deteriorated by the diffusion of magnesium progress to the surface of the deposition and form β phase ($Mg_{17}Al_{12}$) layer on the surface. Thus, it is concluded the aluminum deposition by sputtering is possible to improve the corrosion resistance of the AZ91 magnesium alloy. Further improvement in corrosion resistance can be expected by devising the heat treatment conditions in the future.

STRUCTURAL AND OPTICAL PROPERTIES OF VO_x THIN FILMS

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VO_x thin films were deposited on Corning glass, fused silica and Ti foils by means of rf reactive sputtering from a metallic vanadium target. Argon-oxygen gas mixtures of different compositions controlled by the flow rates were used for sputtering. Temperature of the film substrate was kept constant at 290^{o}C.Influence of the oxygen partial pressure in the sputtering chamber on the structural and optical properties of thin films has been investigated.

Structural properties of as-sputtered thin films were studied by X-ray diffraction at glancing incidence, GIXD. Optical transmittance and reflectance spectra were recorded with a Lambda 19 Perkin-Elmer double specterophotometer over a wide wavelength range from 250 to 2500 nm. Optical constants, extiction coefficient and refractive index as well as the fundamental absorption edge were analyzed.

Thickness of the films as determined from the profilometry was found to be of about 100-200 nm. It has been confirmed that the deposited films are composed mainly of V_2O_5 phase. The estimated optical band gap of 2.5 eV corresponds to V_2O_5. Therefore, it can be concluded that careful control of the sputtering parameters provides films of good quality for various optoelectronic applications.

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THE ANALYSIS OF STRUCTURE FOR THE MULTI-LAYERED OF Ge/TiO_2 FILMS PREPARED BY THE DIFFERENTIAL PUMPING CO-SPUTTERING

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As a candidate of the novel materials for the QDs solar cell, a composite film of anatase-dominant TiO_2 sensitized by Ge nanocrystal (Ge/TiO_2) was presented by S. Abe[2)] et al. Since the optimum deposition condition of Ge and TiO_2 should be different, it is difficult for a conventional sputtering apparatus having one chamber to provide sufficient performance to the composite film. Recently, the differential pumping co-sputtering system (DPCS), which can co-deposit each material under the different atmosphere, was developed. We tried to fabricate the Ge/TiO_2 composite films with the DPCS in order to improve the optical properties. Ge and TiO_2 were deposited on the substrate rotating stepwise under Ar and a mixture of Ar/O_2 atmosphere, respectively. We reported mainly on the following two points in the previous ICPMAT meeting. First, X-ray diffraction patterns revealed that Ge phase with an anatase dominant structure of TiO_2 matrix was successfully obtained by the co-deposition of Ge and TiO_2. Second, onset absorption of the 10.2%Ge/TiO_2 composite film was shifted to about 1.5eV in contrast to the optical absorption edge of 3.1eV for the TiO_2 film with a single phase anatase structure. In the study, the micro structure of these thin films has been evaluated. TEM image revealed that the thin film was alternately layered with TiO_2 and Ge, lattice fringes were observed both of Ge layer and TiO_2 layer. There were portions that lattice fringe of Ge was disturbed near the interface of Ge and TiO_2. X-ray photoelectron spectroscopy elucidated that there were few germanium oxidize and a part with the thin film after annealed.

MICROSTRUCTURE OBSERVATION AND SUPERCONDUCTIVE PROPERTY OF HIGH VOLUME FRACTION MgB_2/ Mg ALLOY COMPOSITE MATERIALS

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In previous work, MgB_2 particle dispersed Al alloy composite materials were fabricated by three-dimensional penetration casting (3DPC) method and investigated their microstructures and superconducting properties. In this work, we fabricated MgB_2 particle dispersed Mg alloy composite materials. The composite materials were fabricated using semi-solid Mg alloy (SS-3DPC) to avoid burning. The composite materials included high volume fraction MgB_2 of particle (40-50 vol.%) and the matrix was used Mg alloy which included different additional elements. The composite materials were able to hot extrusion. The microstructure of these MgB_2 particle dispersed Mg alloy composite materials were investigated by SEM. The distribution of MgB_2 particle was homogeneous in the matrix. The T_C of extruded composite materials determined by electrical resistivity was about 39K.

CHARACTERIZATION OF TiO_2 THIN FILMS PREPARED BY REACTIVE RF MAGNETRON SPUTTERING

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TiO_2 has three types of crystallographic structures: rutile, anatase, and brookite. Among these structures anatase is well known for its higher photocatalytic characterization. Sputtering is one of the methods to fabricate TiO_2 films or coatings. In sputtering deposition process of TiO_2, metal Ti or sintered TiO_2 target is used as deposition source. In this study, we have compared the characteristics of target materials. When TiO_2 target was used, stoichiometric TiO_2 films were deposited under the Ar atmosphere containing 1.0% of oxygen. The highest sputtering rate under this atmosphere was 3.9nm/min at 3.4W/cm^2. But, sintered TiO_2 target is fragile and cannot endure higher density of input power than 3.4W/cm^2. On the other hand, Ti target needs higher oxygen concentration (8%) in sputtering gas atmosphere for obtaining rutile/anatase. Even though Ti target can be input twice power density of 7.9W/cm^2, the highest deposition rate for Ti target was 1.4/nm, which was ~35% of the highest rate for TiO_2 target. Then we have study out the composite target consisting of Ti plate and TiO_2 chips. Using the composite target, stoichiometric TiO_2 films were prepared at high rate of 9.6nm/min at 6.8 W/cm^2 under the atmosphere of Ar/2.5%O_2. Furthermore, we have found that the as-deposited TiO_2 films obtained from the composite target consisted of about 100% anatase, whereas TiO_2 films obtained from other target have rutile dominant structure. The optical band gap energy of the film is determined by using the Tauc plot. The calculated band gap energies for the films deposited by Ti target and composite target were 2.95 and 3.24eV, which are equivalent to that of rutile and anatase structure, respectively.

THE AGE-PRECIPITATIONS STRUCTURE OF Al-Mg-Ge ALLOY AGED AT 473K

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Al-Mg-Ge alloy is one of the age-hardenable aluminum alloy by aging after solution heat treatment. It has been proposed that the age-precipitation of Al-Mg-Ge alloy is different from that of Al-Mg-Si alloy according to our previous works about the microstructure on Al-Mg-Ge alloy over-aged at 523K. For example, the hardness of peak aged Al-1.0mass%Mg_2Ge alloy is higher than that of Al-1.0mass%Mg_2Si alloy. The precipitates in the over-aged samples have been classified as some metastable phases, such as the β'-phase and Type-A precipitates and equilibrium phase of β-Mg_2Ge by TEM observation. There a few reports about microstructure on Al-Mg-Ge alloys observed by TEM for different aging times. The age-precipitations structure of Al-Mg-Ge alloy has not become clear. In this work, TEM observation was investigated the microstructure on Al-1.0mass%Mg_2Ge alloy for difference aging times aged at 473K.

EFFECT OF Sb ON SPHEROIDAL GRAPHITE

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Since the ductile cast iron has the characteristics, such as outstanding mechanical properties, it is broadly used for auto parts, machine structure parts and so on. RE elements are added as spheroidizing treatment. However, it is reported that it promotes growth of the chunkey graphite. Sb is added as a purpose to prevent formation of the chunkey graphite. In this study, the influence of Sb to mechanical property and graphite formation on ductile cast iron is researched by changing quantity of Sb addition. In SEM observation, the surface form of the spheroidal graphite was obtained the coarse surface in base alloy, while the smooth surface was obtained in 0.1Sb. In TEM observation, internal structure was observed the shape of a block with the spheroidal graphite of the base alloy, while the internal structure was observed smoother with the spheroidal graphite in 0.1Sb.

MICROSTRUCTURE OF V_3Ga HIGH Ga CONTENT Cu-Ga/V COMPOSITE SUPERCONDUCTING WIRE

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V_3Ga is a low activation material and is excellent in the High magnetic field characteristic. It attracts attention as wire for nuclear fusion superconducting magnets. Our co-worker, Hishinuma et. al. has established a new route Powder-In-Tube (PIT) process using a high Ga content Cu-Ga compound in order to improve the superconducting property of the V_3Ga compound wire. In this study, we investigated microstructure of this high Ga content Cu-Ga/V composite superconducting wire. The different contrasts of matrix, V-Ga phase and Cu-Ga core were observed by SEM observation in cross section of mono wire. And V-Ga phase was confirmed by SEM-EDS. Thin film sample with V-Ga phase for TEM was fabricated by FIB and observed by TEM in detail.

TEM OBSERVATION OF HPT-PROCESSED EXCESS Mg-TYPE Al-Mg_2Si ALLOYS

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Severe plastic deformation (SPD) techniques, such as equal channel angular pressing (ECAP), accumulative roll bonding (ARB) and high pressure torsion (HPT) have been extensively investigated to achieve. SPD techniques make use of plastic deformation process where no change in the cross-sectional dimension of a work piece occurs during straining. In this work, the effect of HPT on the aging behavior and microstructure in excess Mg-type Al-Mg-Si alloys including Cu are investigated. These alloys were investigated by hardness test and transmission electron microscopy (TEM) observation.

The results show that processing by HPT leads to significant grain refinement with a grain size of 200-250nm. An age-hardening phenomenon is observed at 343K and 373K for the Al-Mg-Si alloys with HPT. Some precipitates were observed on grain boundaries.

TEM OBSERVATION OF AGE-HARDENING PRECIPITATION IN Mg-Gd-Y ALLOYS AS DIFFERENT Gd/Y RATIO

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Magnesium alloys containing rare earth elements are known to show good heat resistance. The Mg-Gd alloy shows good age-hardenability, and the Mg-Gd-Y alloys have been developed for practical Mg alloys by Kamado et. al. to reduce the density of alloy and these alloys have a good creep resistance, even 523 - 573 K. The precipitation sequence in Mg-Gd-Y alloys aged at 473K has been investigated using transmission electron microscopy (TEM). It is described as super-saturated solid solution (S.S.S.S.)→β”(DO_{19})→β’(cbco)→β_1(fcc)→β(fcc). However, the precipitation behavior of the Mg-Gd-Y alloys at early stage of aging after quenching was not understood clearly. In this study, the early stage of aging in Mg-Gd-Y alloys has been observed by TEM, high angle annular dark field - scanning transmission electron microscopy (HAADF-STEM) and calculations of images and electron density and bond overlap population (BOP) by first principal to understand the origin of precipitation in this alloy. The small hexagon of 0.37 nm is the first precipitate in this alloy, and this is the evidence of short range ordering of DO_{19} structure. This is referred as the pre β”-phase. In the peak aged condition, β’ phase with bco structure was mainly observed.

INFLUENCE OF HEAT-TREATMENT ON THE STRUCTURE AND MECHANICAL PROPERTIES OF AlN/SiCN COMPOSITE COATINGS

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The performance of coatings for cutting tools depends highly on the hardness and the oxidation resistance at elevated temperatures[1)]. We reported that AlN/SiCN composite coatings by r.f.-reactive sputtering method using a facing target-type sputtering (FTS) obtained a maximum hardness of above 30 GPa in wide extent of composition. The aim of this work is to investigate the influence of heat-treatment in the various atmospheres including air on the structure and mechanical properties of AlN/SiCN composite coatings. AlN/SiCN composite coatings were deposited by r.f.-reactive sputtering using a composite target consisting of Al plate (160mm×100mm×10mm) and 16 pieces of SiC chips (10mm×10mm×2mm) when a gaseous mixture at Ar and N_2. The indentation hardness (H_{IT}) of a AlN/SiCN composite coating (Ar/N_2=10/3sccm) increased from 29 GPa to 34 GPa by annealing in air at 700~800^oC for 1 hour. But H_{IT} of another AlN/SiCN composite coating (Ar/N_2=10/10sccm) decreased monotonically by annealing over 700^oC. H_{IT} of other AlN/SiCN composite coating (Ar/N_2=10/17sccm) kept by annealing up to 800^oC, then decreased from 28 GPa to 19 GPa by annealing at 900^oC. X-ray diffraction (XRD) patterns of AlN/SiCN composite coating after annealing indicated the only peeks of hexagonal (B4) structured AlN phase without any other peeks.

[1] R. Forsén et. al., Thin Solid Films 534 (2013) 394.

MECHANICAL PROPERTIES AND MICROSTRUCTURE OF AlN/SiCN NANOCOMPOSITE COATINGS PREPARED BY R.F.-REACTIVE SPUTTERING

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Transition metal nitrides like TiN, ZrN, CrN are adopting as hard protective coatings of mechanical tools for their wear and corrosion resistance and high melting point [1]. However, the development of hard protective coatings consisting of light elements such as Si, Al, C, N have been expected in order to conserve rare metal resources. In this work, AlN/SiCN composite coatings were deposited by r.f.-reactive sputtering method using a facing target-type sputtering (FTS) apparatus with composite targets consisting of Al plate and SiC chips in a gaseous mixture of Ar and N_2, and investigated their mechanical properties and microstructure. The indentation hardness (H_{IT}) of AlN/SiCN coatings prepared from composite targets consisting of 8 ~ 32 chips of SiC and Al plate showed the maximum value of about 29 ~ 32 GPa at a proper nitrogen gas flow rate. X-ray diffraction (XRD) patterns for the AlN/SiCN composite coatings indicated the presence of the only peeks of hexagonal (B4) structured AlN phase. Cross sectional view TEM observation clarified that the coatings consisted of columnar structure in single layer AlN coatings. On the other hand, microstructure of AlN/SiCN composite coatings changed from column to equiaxed structure with increasing SiCN content. HR-TEM observation clarified that the composite coatings consisted of very fine equiaxial grains of B4 structured AlN phase and amorphous phase.

[1] D. Valerini et. al., Thin Solid Films 538 (2013) 42–47

EFFECT OF Zn/Mg ON MICROSTRUCTURE AND MECHANICAL PROPERTIES IN 7XXX Al ALLOYS

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7XXX Al alloy has been known as one of the aluminium alloys with the good age hardening ability and the high strength among commercial aluminium alloys. In this study, hardness measurement, tensile test, SEM observation and TEM observation have been performed in order to understand the effect of Zn/Mg ratio on age hardening behaviour in Al-Zn-Mg alloys. It can be seen from hardness measurement that the peak hardness increased with increasing the amount of Zn and Mg.

Tensile test was performed for the peak aged samples. It can been seen that UTS increased with increasing the amount of the Zn and Mg. Their elongation decreased with increasing the amount of the Zn and Mg. Intregranular fracture was observed in low amount of Zn and Mg alloy, and Transgranular fracture was observed in high amount alloy. TEM observation was performed for peak aged samples. The size of precipitates became finer and the number density increased with increasing Zn and Mg contents. T' and η1 phases were observed in low Zn/Mg alloy, although η' phase was observed in high Zn/Mg alloy.

EFFECT OF A SMALL AMOUNT OF TRANSITION METALS ADDITION AGING PRECIPITATION OF Al-Mg-Si ALLOYS

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The addition of transition metals to Al-Mg-Si alloys affects the mechanical properties.Transition metals are usually added to Al-Mg-Si alloys for grain refinement to modify their elongation. Ni-added alloy form some dispersoids as Al_xNi_y ,and peak hardness of this alloy increases peak higher than that of base alloy. Moreover, peak hardness of no dispersoids-free alloy with a small amount of Ni is higher than some intersoids alloys that in alloys containing Ni higher than 0.1%. Mn-added alloys form some dispersoids as $Al_xMn_ySi_z$,and peak hardness of these alloys decrease lower than that of base alloy.But, peak hardness of dispersoid-free alloy with a small amount of Mn is higher than that of base alloy. In this study, the aging behavior of these alloys has been investigated by TEM observations to understand the effect of a small of Ni or Mn addition on aging precipitation.

MICROSTRUCTURE OF OXIDE INSULATOR COATING LAYER PREPARED BY MOCVD PROCESS

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In breeding blanket system of nuclear fusion reactor needs to develop advanced type of coating to leak control of tritium and reducing magneto hydrodynamic (MHD) pressure drop. In breeding blanket system, material needs to fulfill five conditions: 1. Not break down at high temperature; 2. Low reactivity with Li as a coolant; 3. High electrical resistivity; 4. High permeation control of tritium; 5. High electrically insulating coating of 2μm or more. It has been reported that Er_2O_3 has excellent electrical resistance and a permeation control effect from various ceramic materials. Hishinuma et. al. succeeded in forming Er_2O_3 film by metal organic chemical vapor deposition (MOCVD) process as a new technology for large area coating on broad and complicated shaped components. From SEM observation, Er_2O_3 was observed granular structure that various size and looked like line up by vapor for MOCVD process.

TEM OBSERVATION FOR PRECIPITATES STRUCTURE OF AGED 7XXX SERIES Al ALLOYS ADDITION OF Cu OR Ag

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Al-Zn-Mg alloy has been known as one of the aluminum alloys with the good age-hardening ability and the high strength among commercial aluminum alloys. The mechanical property of the limited ductility, however, is required to further improvement. In this work, three alloys, which were added Cu or Ag into the Al-Zn-Mg alloy, were prepared to compare the effect of the additional elements on their aging behavior. Ag or Cu added alloy showed higher maximum hardness than Ag or Cu free alloy. The number density of the precipitates in Ag or Cu added alloy increased than Ag or Cu free alloy. The GP(Ⅱ) zone and η' phase were observed in all alloys peak-aged at 423K, although GP(Ⅰ) zone was confirmed in the Cu added alloy.

REDUCTION OF NICKEL SULFIDE NiS

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The increasing demand of the modern world on hydrogen as a source of clean, renewable energy entails the search for new methods for the preparation of this gas on an industrial scale. One such promising method is the electrolysis of aqueous alkali solution. A problem limiting the applicability of the method on a larger scale is to provide a respective electrode materials with low hydrogen evolution overpotential, thereby reducing energy consumption of the process. One of the best electrode materials is nickel and its alloys having high electrochemical activity and stability in the operating conditions. The performance of the electrodes can also be improved by increase in surface area. There are several methods of preparation such porous nickel-based materials, among others the sequential oxidation and reduction of metallic powder deposits. The present paper describes a first step toward new way of preparation nickel with highly developed surface area by sulfidation and reduction of metallic substrate. Nickel sulfide NiS was chosen as a starting material (precursor). The sulfide, having the dendritic needle-like morphology, was obtained by sulfidation of pure nickel foils in an atmosphere containing sulfur vapors, under properly selected conditions. The goal of the study was to investigate the possibility of receiving metallic nickel with morphology corresponding to the starting material through the reduction of NiS precursor.

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CROFER 22 APU FERRITIC STAINLESS STEEL

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The main goal of the research was to expand the knowledge on microstructure and mechanical properties of the oxidized Crofer 22 APU stainless steel, what is necessary to conduct successful tribological measurements. Microstructure and hardness were investigated on a raw steel. Scratch properties were investigated before and after high temperature oxidation.

Microstructural observations and hardness coefficient measurements were carried out, with a special emphasize put on the analysis of non-metallic inclusions. EDS analyses confirmed that the non-metallic inclusions are titanium nitrides (TiN) containing a phase enriched with carbon, what leads to formation of complex titanium carbonitrides. The hardness coefficient of inclusions was about one order of magnitude higher than that of the matrix (285.51 and 2402 HV, respectively). To examine adhesion of oxide scale formed on steel the scratch test were performed. The test was carried out before and after isothermal oxidation at 800^{o}C for 400 hours in laboratory air atmosphere. Obtained results, combined with the planned tribological measurements, should allow complete assessment of wear resistance properties of the scale formed on the Crofer 22 APU substrate.

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SURFACE TOPOGRAPHY INVESTIGATION OF $(La,Sr)(Co,Fe)O_3$ FILM PREPARED BY PULSED LASER DEPOSITION (PLD) ON FERRITIC STAINLESS STEEL

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Topographic studies of $(La,Sr)(Co,Fe)O_3$ film have been carried out. The film was deposited on the stainless steel substrate by pulsed laser deposition (PLD) technique. The film XY profiles (i.e thickness, rms roughness and refractive index) was determined by optical profilometry (PO) and scanning spectroscopic ellipsometry (SSE) methods. Using the first method a map of the local reflectance of the small surface area ($10^2 mm^2$) can be obtained, whereas changes in the polarization light beam of reflected from the film upon the surface position can be determined by the second method. It was determined that the mean thickness of the film was about 1137 nm and the thickness dispersion of the film was less than 4 nm. This indicates that the film is uniform across the surface of the sample. The combined PO and SSE investigations have been used to determine the root mean square (rms) roughness and autocorrelation length of films and surfaces. The Fourier transform analysis of layer images was applied to determine correlation between upper and lower film surface obtained from PO and SSE studies. OP investigation enabled one to find many interesting features concerning film surface. From the image analysis, the most important statistic parameters of surface, such as waviness and their high distribution function was determined.

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FABRICATION AND CHARACTERIZATION OF CATHODE-ELECTROLYTE GRADIENT SYSTEM FOR USE IN PROTON-CONDUCTING FUEL CELLS

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Proton-conducting solid oxide fuel cells (PCFC) are very promising energy generators distinguished by high efficiency and very low emission of toxic gas. An important aspect is to select a suitable cathode material working with high temperature proton conductor electrolyte. The most desirable cathode material for protonic fuel cell should present both electronic and protonic conductivity which allows for the expansion of the triple phase boundary from the electrode/electrolyte/gas interface to the cathode bulk. One way of achieving such type of conductivity is to produce composite cathode consisting of both protonic and electronic conducting phases. In addition, use of a composite cathode reduces problems with the thermal expansion mismatch between the electrode and the electrolyte. A potential solution to these problems is the use of suitable materials of the gradient structure. In this study, a cathode-electrolyte gradient system was obtained by using $Ba_{0.99}Ce_{0.95}Dy_{0.05}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as the electrolyte and cathode material respectively. The test system was composed of ceramic layers with differing content of electrolyte and cathode materials placed between pure electrolyte and cathode pellets. To verify the chemical stability of the system after oxidation in 1273K for 100 hrs in air, XRD analysis was carried out. The results indicated that no secondary phases were formed. Measurement of electrical properties of the sample were carried out by electrochemical impedance spectroscopy method which indicated improvement of electrical properties compared to the conventional cathode-electrolyte system.

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ELECTRICAL PROPERTIES OF INDIUM AND YTTRIUM-DOPED BARIUM CERATE-BASED COMPOUNDS FOR USE AS CERAMIC FUEL CELL ELECTROLYTES

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The objective of this work is to compare the electrical properties of $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ (BCY15), $BaCe_{0.70}In_{0.30}O_{3-\delta}$ (BCI30) and a composite material obtained by mixing 20% BCY15 with 80% $Ce_{0.85}Y_{0.15}O_{2-\delta}$ (YDC15). BCY15 and YDC15 were synthesized by co-precipitation, whereas BCI30 was obtained using the solid-state reaction method. Bulk samples were formed at 50 bar. BCY15 and the composite sample (Y80B20) were then isostatically pressed at 250 MPa and sintered at 1500^{o}C, whereas BCI30 was isostatically pressed at 300 MPa and sintered at 1450^{o}C for 5 hrs. Electrochemical impedance spectroscopy (EIS) was used to determine the electrical properties of the samples in both air (p_{O2} = 0.21 atm) and Ar-5%H_2 atmospheres. The highest conductivity values were determined for BCY15. These values are in the order of magnitude of 10^{-5} - 10^{-3} S/cm in air atmosphere in the temperature range 200-400^{o}C. On the other hand, the electrical conductivity values obtained for Y80B20 in both atmospheres in the low temperature range (200-450^{o}C) are in the order of magnitude of 10^{-7} - 10^{-3} S/cm. It was determined that the conductivity values for this sample in the low temperature range are slightly higher in Ar-5%H_2 atmosphere that in air. Consequently, it can be concluded that the compounds exhibit significant H^{+} and O^{2-} electrical conductivity at temperatures above 500^{o}C for use as potential ceramic fuel cell electrolytes.

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EFFECT OF THE GADOLINIUM ADDITION ON THE ELECTRICAL PROPERTIES OF TETRAGONAL ZIRCONIUM DIOXIDE

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The aim of this work was to obtain 3YSZ materials doped with gadolinium in amount 0.25; 0.5; 1.0 at %, which may be used as electrolytes in intermediate temperature solid oxide fuel cells (IT-SOFC). It was determined that gadolinium addition affects the electrical and structural properties of 3YSZ. The prepared materials have high porosity and no influence of gadolinium addition on grain size was observed. The results of this work indicate that electrical conductivity of grains interiors is typical for the tetragonal zirconium dioxide. On the other hand, gadolinium addition had a clear effect on the electrical conductivity of the grain boundaries. Also, it was found that diffusion processes occurred during annealing for an long period of time in hydrogen atmosphere at the grain boundaries. It was found that 3YSZ containing 0.25 at % Gd is the most promising solid electrolyte material for IT-SOFC.

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THE INFLUENCE OF ALUMINA ADDITION ON THE PERFORMANCE OF 3YSZ MATERIAL

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Yttria-stabilized zirconia (YSZ) is the most well known ceramic-oxide material employed as a solid oxide fuel cell (SOFC) component; either as a solid electrolyte or an anode cermet material. According to literature, the addition of Al_2O_3 to the YSZ matrix influences the conductivity of samples by increasing their grain boundary conductivity as a result of removing SiO_2. The properties of traditionally obtained (by mechanically mixing oxides) Al_2O_3-3YSZ composite and materials obtained by citrate and impregnation methods were compared with the properties of SiO_2-3YSZ. The materials were characterised by X-ray diffraction, scanning electron microscopy (SEM) observations combined with energy dispersive X-ray spectroscopy (EDS) analysis, porosity and impedance spectroscopy measurements. The results show that SiO_2-3YSZ materials have lower conductivity than pure 3YSZ and that the addition of alumina (regardless of the method) improve electrical properties of the materials. At the same time, electrical measurements prove that citrate and impregnation methods lead to the synthesis of Al_2O_3 – 3YSZ materials with better ion conduction than composites obtained by the traditional method.

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ELECTRICAL PROPERTIES OF THE SELECTED RARE EARTH OXYCHLORIDES

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Rare earth oxychlorides (REOCl) are novel functional materials that have many potential uses, e.g. as solid electrolytes in electrochemical devices. According to literature, some of their properties were subjects of preeliminary studies, e.g. paramagnetical susceptibility and structural stability. Up to now, only one compound from the whole range of REOCl, namely lanthanum oxychloride (LaOCl), was investigated from the viewpoint of its electrical properties. The aim of these studies was to determine the dependence between the ionic radius of RE elements and the electrical, as well as structural properties of REOCl compounds. The selected REOCl (LaOCl, NdOCl, GdOCl, HoOCl, YbOCl) were synthesized via reactions between commercially available rare earth oxides and ammonium chloride at an elevated temperature in neutral argon atmosphere. Initially, calcination and sintering conditions were chosen according to literature data and then modified in order to obtain one-phase materials. The phase compositions, as well as crystallographic structures, were examined by XRD analysis. The electrical conductivities, as well as activation energies of the materials, were determined by electrochemical impedance spectroscopy (EIS).