SYMPOSIUM PM06

Advances in Intermetallic-Based Alloys for Structural and Functional Applications
November 26 - November 29, 2018

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* Invited Paper

SESSION PM06.01: Titanium Aluminides I
Session Chairs: John Lewandowski and Masao Takeyama
Monday Morning, November 26, 2018
Hynes, Level 1, Room 104

8:30 AM *PM06.01.01
Development and Application of Titanium Aluminides Wilfried G. Smarsly[1], Helmut Clemens[2] and Svea Mayer[2]; [1]MTU Aero Engines, Muenchen, Germany; [2]Metallkunde und Werkstoffprüfung, Montanuniversität Leoben, Leoben, Austria.

Intermetallic Titanium Aluminid based alloys are considered for high-temperature aero and automotive engine applications. The advantage of this class of innovative high-temperature materials is their low density in combination with good strength and creep properties up to 850°C. A drawback, however, is their limited damage tolerance at room temperature, which is reflected in a low plastic fracture strain and fracture toughness. Advanced engineering Titanium Aluminid alloys are complex multi-phase materials which can be processed by ingot or powder metallurgy. Engine components can be manufactured by casting as well as additive manufacturing, e.g. electron beam melting. Each ingot production process leads to specific microstructures which can be optimized by thermo-mechanical processing, e.g. isothermal or hot die forging and subsequent heat treatments. Thermo-mechanical processing can provide balanced mechanical properties, i.e. a minimum ductility at room temperature as well as sufficient creep strength at elevated temperature. In order to achieve this goal, the knowledge of the occurring solidification processes and phase transformation sequences is essential. Therefore, thermodynamic calculations were conducted to predict the phase diagram of engineering TiAl alloys. After experimental verification, these phase diagrams provided the basis for the development of heat-treatments. To account the influence of deformation and kinetic aspects sophisticated ex- and in-situ methods have been employed to investigate the evolution of the microstructure during thermo-mechanical processing. For example, in-situ high-energy X-ray diffraction was conducted to study dynamic recovery and recrystallization processes during hot-deformation tests. Novel high-strength Titanium Aluminid based alloys, such as TNM alloys have been developed in the last decade to meet the advanced requirements of aero engines.These alloys are characterized by a high content of β-stabilizing alloying elements, such as Nb and Mo. Because Nb and Mo represent the decisive alloying elements, this alloy family, based on the γ-TiAl phase, has been named "TNM alloys" in order to distinguish them from the well-known and even stronger "TNB alloys" which rely on a high Nb concentration and small additions of B and C. At room temperature, strength levels > 1000 MPa can be achieved in advanced TiAl alloys by appropriate thermo-mechanical processing and subsequent heat treatments. It is important to note that also high temperature properties, such as creep resistance, were considerably improved, e.g. by implementation of precipitation hardening, which further extend the application range of Titanium Aluminid based alloys.

9:00 AM PM06.01.02
Design Approaches and Achievements of Novel Wrought TiAl Alloys for Jet Engine Applications Masao Takeyama[2, 1]; [1]Tokyo Institute of Technology, Tokyo, Japan; [2]Materials Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan.

Innovation of structural materials is urgently being required for contribution to worldwide issues on energy, environment, and high performance jet engine development with larger thrust-to-weight ratio is one of them, since more than 30,000 new airplanes are to be produced by 2030.
A five-year National project of "*Structural Materials for Innovation* (SM[4]I)" in *Cross-ministerial Strategic Innovation Promotion Program* (SIP) starting from 2014 is currently going on in Japan. In this project of SM[4]I, a focus is placed on innovative structural materials applicable for jet engines, where author at Tokyo Tech is committed to as a technical leader and take responsibility for alloy design and development of TiAl alloys in collaboration with other universities (Hokkaido Univ, Osaka Univ.) and industries (Kobe Steel, Ltd and IHI Co.). In this talk, design approaches and achievements for the development of wrought TiAl alloys to be used for LPT and HPC blades are presented. First, we built up a new database for phase diagram calculations in multi-component systems of the alloys, including both substitutional and interstitial elements. In case of Ti-Al-M_1-M_2 quaternary systems, for example, we optimize the interaction parameters to calculate the phase diagram in good agreement with experimentally determined phase diagram, by taking into considerations of temperature, aluminum and M_1/M_2 concentration dependencies in the four phases of β-Ti, $α_2$-Ti_3Al, α-Ti and γ-TiAl phases. Based on the phase diagram calculations, we successfully proposed model alloys with excellent hot workability even at higher strain rate and room temperature ductility of more than 1%. It should be noted that an introduction of bcc b-Ti phase and microstructure design using a unique phase transformation pathway of β+α→α→β+γ in the multi-component systems makes it possible to have excellent properties in both process and service temperatures.
We revealed the alloy with lamellar microstructure decorated by β/γ duplex microstructure at the lamellar colony boundaries show better crack initiation

and propagation resistance than that with fully lamellar microstructure. The detailed microstructure control method using the phase transformations and toughening mechanism will be presented.

Part of this study was carried under the research of SIP in JST (Japan Science and Technology Agency).

9:15 AM PM06.01.03
Phase Transformation and Microstructure Evolution during Continuous Heating of an Intermetallic β-homogenized Ti-43Al-7Mo (at.%) Alloy Petra Erdely[1], Peter Staron[2], Andreas Stark[2], Thomas Klein[1, 3], Helmut Clemens[1] and Svea Mayer[1]; [1]Department of Physical Metallurgy and Materials Testing, Montanuniversitaet Leoben, Leoben, Austria; [2]Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; [3]Now with: Materials Center Leoben Forschung GmbH, Leoben, Austria.

Intermetallic γ-TiAl based alloys provide promising engineering properties for lightweight high-temperature applications. Hierarchical structures that comprise microstructural constituents on the nanometer scale have received much attention in recent years, as research suggests that they can further improve the performance of these alloys. In the present work, a ternary Ti-43Al-7Mo (at.%) model alloy is investigated. This β/γ alloy can be homogenized in the β single-phase region at 1450 °C, while water quenching prevents further large-scale phase transformations. Subsequent reheating to temperatures above 500 °C provokes the formation of fine γ particles on the sub-micron level. As these particles appear homogeneously distributed throughout the $β_o$ matrix and form a continuous network after long annealing times, the microstructure of the alloy can, thus, be substantially refined. However, the exact mechanisms of this phase transformation are still not fully understood. The present work addresses these mechanisms through the application of a variety of characterization techniques. In a dilatometer setup at a synchrotron radiation source, β-homogenized specimens were heated at various constant rates ranging from 10 to 400 K/min. *In situ* high-energy X-ray diffraction was used to study the structural changes in the prevalent phases. The combination of *in situ* small-angle X-ray scattering and *ex situ* atom probe tomography allowed the analysis of the early stages of the precipitation process by characterizing the nanometer-scale precipitates in terms of size, shape and chemical composition. The final microstructure of selected heat-treated specimens was analyzed using scanning electron microscopy. In sum, the experiments offered deep insights into the functioning and the kinetics of the thermally activated γ growth sequence in a β-homogenized Ti-Al-Mo alloy. The detailed understanding of this phase transformation is an essential prerequisite for the design of refined microstructures in β/γ alloys without the necessity for prior hot working.

9:30 AM PM06.01.04
Improvement of Mechanical Properties of TiAl Alloys Fabricated by Electron Beam Melting though Microstructure Control Ken Cho[1], Masahiro Sakata[1], Takumi Fukuoka[1], Jong Yeong Oh[1], Hiroyuki Yasuda[1], Mitsuharu Todai[2], Takayoshi Nakano[1], Ayako Ikeda[3], Minoru Ueda[4] and Masao Takeyama[5]; [1]Osaka University, Suita, Japan; [2]Institute of Niihama National College of Technology, Niihama, Japan; [3]National Institute for Materials Science, Tsukuba, Japan; [4]Metal Technology Co. Ltd., Tokyo, Japan; [5]Tokyo Institute of Technology, Tokyo, Japan.

TiAl alloys are candidate materials for low pressure turbine blades of a jet engine due to their low density and excellent strength at high temperatures. Electron beam melting (EBM) is one of the suitable manufacturing processes for the TiAl alloys. Because it is possible to fabricate 3D products easily by adding layer-on-layer of materials. We found the TiAl alloys fabricated by EBM have unique layered microstructure consisting of equiaxed gamma grains regions (gamma bands) and duplex-like regions perpendicular to building direction. This layered microstructure is formed by repeated thermal effect from the melting pool.

In this study, the influence of the layered microstructure on mechanical properties of the TiAl alloys was investigated focusing on the morphology of the gamma bands. To control the layered microstructure, the alloys were fabricated by EBM at various conditions. Moreover, some of the as built alloys were subjected to heat treatments including hot isostatic pressing (HIP) at various temperatures. The width of the gamma bands was affected not just by the electron beam scan speed but also by the heat treatments. The room temperature ductility of the alloys increased with increasing the width of the gamma bands and reached a maximum at approximately 3%. The alloys with suitable morphology of the gamma bands show also excellent fatigue strength. These results indicate that the alloys with the unique layered microstructure have a great potential for aerospace applications.

9:45 AM PM06.01.05
Micro-Mechanical Response and Texture Evolution of Ultrafine-Grained Titanium Aluminide Processed by High-Pressure Torsion Megumi Kawasaki[1], Jae-Kyung Han[1], Xi Li[2, 3], Rian Dippenaar[2] and Klaus-Dieter Liss[4, 3, 2]; [1]Oregon State University, Corvallis, Oregon, United States; [2]University of Wollongong, Wollongong, New South Wales, Australia; [3]Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales, Australia; [4]Guangdong Technion - Israel Institute of Technology, Shantou, China.

The present study applies a strategy of grain refinement on a γ-based Ti-45Al-7.5Nb intermetallic compound through high-pressure torsion (HPT) processing for 5 and 10 turns under a compressive pressure of 6.0 GPa at room temperature. Successful grain refinement was introduced in the duplex microstructure to have ultrafine laths with thicknesses of 40-100 nm after 10 HPT turns. Exceptional hardness is recorded after the severe plastic deformation and the X-ray diffraction analysis confirmed the occurrence of phase transformation from γ-TiAl to $α_2$-Ti_3Al in the alloy. The close investigation demonstrated that hardness and texture evolution vary gradually from the sample surfaces to the core, thereby exhibiting a heterogeneous microstructure. Macroscopic plastic flow is estimated thorough the micro-mechanical responses by the nanoindentation technique for the TiAl alloy. This study demonstrates the promising feasibility of HPT processing for improving essential mechanical properties in the TiAl.

10:00 AM BREAK

10:30 AM *PM06.01.06
Industrial Recycling of Valuable TiAl Revert Volker Guther; GFE Metal & Materials GmbH, Nuremberg, Germany.

Low Pressure Turbine blades made of TiAl alloys are being used in three civil aircraft engine families (GEnx, PW1000GTF, LEAP). The production process of TiAl semi-finished parts is based on three technological pathways:
VAR ingot metallurgy, VAR Skull Melter homogenization and subsequent investment casting to oversized components followed by mechanical machining
VAR ingot metallurgy, VAR Skull Melter homogenization and subsequent centrifugal casting in permanent moulds to small sized feed stocks for either forging and mechanical machining or direct mechanical machining
Plasma Arc Cold Hearth Melting to small sized ingots for direct mechanical machining
In both processing routes b) and c), a substantial amount of valuable TiAl revert is being generated during the different processing steps. An industrial recycling pocess based on Vacuum Induction Skull Melting with subsequent centrifugal casting according to the technological pathway b) has been developed and commissioned at GfE. Appropriate revert preparation technologies prevent a detectable impurity pick-up from previous processing steps even for multiple use of revert. The corresponding revert preparation and revert conversion technology is approved and validated for the production of pre-materials for components for aircraft engines. The presentation addresses the origin of revert and the appropriate revert preparation technology. The recycling process via Induction Skull Melting is being introduced. Resulting products are indistinguishable from products resulting from the virgin

production route via VAR Skull Melting with regard to chemical composition and microstructure.

11:00 AM PM06.01.07
Introduction of YSK-TiAl, Novel Wrought Alloy with High Strength and Advanced Productibility <u>Keiji Kubushiro</u>, Yutaro Ota, Yohei Sakakibara, Shin Usui, Satoshi Takahashi, Kotaro Tagawa and Masanobu Baba; IHI Corp, Yokohama, Japan.

To evaluate forgeability for wrought TiAl alloy (YSK alloy : Ti-43Al-9(V, Nb)-0.2B), greeble test and compression test were carried out. As a result, it was confirmed that deformation at (β+α) two-phase region promoted recrystallization of α phase and recrystallization was easily developed as grain size was smaller. In addition, (β+α) two-phase region in YSK alloy was larger than the others. Hot-forging was performed on the condition revealed by above tests, and then mechanical properties of heat-treated samples were investigated. Tensile strength and creep strength of YSK alloy were equal to or higher than the other alloys reported so far.
DKth at R.T was about 10 MPa√m. As to forgeability, extrusion, upset, and hot-die-forging at high speed succeeded with existing facilities. At last, more than 200 blades were manufactured by the established method.

11:15 AM PM06.01.08
New Atomic Relaxation Mechanism Discovered in Nano-Lamellar γ-TiAl Leire Usategui[3], Maria L. No[4], Thomas Klein[2], Svea Mayer[1], Helmut Clemens[1] and <u>Jose San Juan</u>[3]; [1]Montanuniversität Leoben, Leoben, Austria; [2]Materials Center Leoben Forschung GmbH, Leoben, Austria; [3]Fisica Materia Condensada, Universidad del Pais Vasco, Bilbao, Spain; [4]Fisica Aplicada II, Universidad del Pais Vasco, Bilbao, Spain.

Two different families of γ-TiAl intermetallics are already flying as blades of the low-pressure turbine in some engines of commercial aircraft, and considerable effort is being devoted to improve their performances. Here we focus on the family named TNM$^+$, which is based on the TNM alloy but containing specifically designed amounts of C and Si in order to optimize the performances. The goal is to increase the creep resistance allowing to extent the working temperature range, and to this purpose a fully nano-lamellar microstructure was developed through thermal treatments.
In the present work we study at high temperature the mobility of defects controlling the mechanisms responsible for creep. However, the study is approached through mechanical spectroscopy by measuring the internal friction (IF) spectra between 300 and 1350ºC. On one hand, the high temperature background (HTB) of the IF is closely related to creep behavior [1], and on the other hand, the relaxation peaks of the IF spectra offer valuable information about the atomic diffusion mechanisms involved in creep [2,3]. In particular, the developed nano-lamellar microstructure allow us to discover and analyze a new relaxation peak, which remains hidden in between the IF peak associated to Ti diffusion in α_2-Ti$_3$Al phase [2] and the HTB. We have measured the IF spectra at different frequencies and performed a deep analysis to decompose the IF spectra into the different contributions and isolate the relaxation corresponding to each individual atomic mechanism. This way we measured the activation energy of the hidden relaxation, E_a=3.7 eV, which is attributed to the Aluminum diffusion in γ-TiAl phase. Moreover, a new atomic relaxation mechanism is proposed to explain the characteristic of the observed IF peak. Finally, the importance of the discovered relaxation is discussed in terms of its relationship with the atomic diffusion processes involved in creep.

11:30 AM PM06.01.09
Density Functional-Based Kinetic Monte Carlo Approach to Ni Pipe Diffusion <u>Luke Wirth</u>[1], Amir A. Farajian[1] and Christopher Woodward[2]; [1]Mechanical and Materials Engineering, Wright State University, Dayton, Ohio, United States; [2]Air Force Research Laboratory, Dayton, Ohio, United States.

Pipe diffusion along dislocations in metals can occur at faster rates than in bulk regions, expediting creep and contributing to device failure. We use density functional theory methods to calculate the vacancy-mediated diffusion coefficient along a <1 -1 0> screw dislocation in FCC nickel. A lattice Green's function technique is used to accurately configure the atomic structure surrounding the dislocation core. Vacancy hop rates within this region are calculated using principles of transition state theory with activation energy barriers and vibrational properties obtained from our ab initio framework. A kinetic Monte Carlo model then uses these rates to describe mass transport within the region on representative timescales at various temperatures.

SESSION PM06.02: Silicides and Ultra-High Temperature Alloys
Session Chairs: Martin Heilmaier and Kyosuke Yoshimi
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.02.01
Alloy Design of Refractory BCC-T$_2$ Silicide-B2 Aluminide Multicomponent-Multiphase Alloys <u>Seiji Miura</u>, Satoshi Takizawa and Ken-ichi Ikeda; Hokkaido University, Sapporo, Japan.

Refractory-metal based materials have attracted attentions for many years because of the increasing demand for high temperature components. In order to obtain such materials having superior properties for high temperature use, multicomponent-multiphase alloys are required. Authors have conducted studies on the mechanical and physical properties of BCC solid-solution phase, M_5Si_3-T_2 silicide phase and B2 aluminide phase, together with phase equilibrium among these constituent phases.
Authors have conducted the investigation on the effects of various additive elements on the strength and deformability of BCC solid solution. As (Nb, Mo)$_5$(Si, B)$_3$ phase dispersion in Nb-Mo BCC solid-solution matrix has been studied by various researchers, we also try to understand the phase stability of T_2 phase in alloys. Although silicide phases including (Nb, Mo)$_5$(Si, B)$_3$ show superior oxidation resistance, we have focused on B2-aluminide coating because B2-NiAl coatings have been used for commercial Ni-based superalloys. To realize a three-phase alloys composed of refractory BCC, T_2 silicide and B2 aluminide, phase equilibrium in ternary, quaternary and higher-order phase diagrams are experimentally investigated. Among them, brittle compounds such as Nb(Ni, Al)$_2$ Laves phase form at the interphase boundary between NiAl and Nb-based alloys during high temperature heat-treatment. To avoid the formation of Laves phase, both the B2 phase composition and the BCC alloy composition were optimized based on the phase diagrams such as Nb-Al-Pd and Nb-Mo-NiAl, then a composition area at which BCC solid-solution phase equilibrates with B2 aluminide was found in Nb-Mo-Ni-Al-Pd quinary system.
By the systematic investigation, it was found that the atomic size ratio of constituent elements is still an important key to understand the stability of ternary Laves phases including Al. For a further understanding of the substitution behavior of elements in the Laves phase, electronic structure calculations based on the density functional theory (DFT) was performed on the alloy system including Si.
This work was supported by the Advanced Low Carbon Technology R&D (ALCA) program of the Japan Science and Technology Agency (JST).

2:00 PM PM06.02.02
Role of Mo Solid Solution on Ultrahigh-Temperature Tensile Creep Deformation of MoSiBTiC Alloy <u>Kyosuke Yoshimi</u>[1], Shiho Y. Kamata[1], Shunichi Nakayama[1], Sojiro Uemura[2], Sadahiro Tsurekawa[2], Gunther Eggeler[3] and Kouichi Maruyama[1]; [1]Tohoku University, Sendai, Japan; [2]Kumamoto University, Kumamoto, Japan; [3]Ruhr-University Bochum, Bochum, Germany.

A Mo-Si-B-based alloy reinforced by TiC (65Mo-10Ti-5Si-10C-10B (at.%)) shows high creep resistance estimated over the rupture time of 1000 h under 137 MPa at 1350°C and relatively good room-temperature fracture toughness over 15 MPa(m)$^{1/2}$. The excellent mechanical properties arise from the high strength of Mo_5SiB_2 (T_2) and TiC, the good ductility of Mo solid solution, and the microstructural configuration of these phases. Under creep deformation, the resistance of Mo solid solution would be one of key factors controlling the overall creep strain of the material and the interfacial sliding between these phases would be the other factor. In this paper, the role of Mo solid solution on ultrahigh-temperature tensile creep deformation is addressed for the MoSiBTiC alloy. The microstructural continuity of Mo solid solution was analyzed in terms of the percolation probability. It was clarified by the percolation probability analysis that both the Mo solid solution and brittle phases (T_2 and TiC) were not 100%-continuous in the microstructure. EBSD and TEM observations for ruptured specimens presented dynamic recrystallization in Mo solid solution due to heavy plastic deformation during creep but much less plastic deformation in the brittle phases. These results represent that the creep strain was given by the dislocation creep of Mo solid solution and the interfacial sliding between the phases. The apparent activation energy of creep was estimated to be about 560 kJ/mol from the Arrhenius plot of the logarithm of the minimum creep rate against inverse temperature. The value is much higher than the activation energy of the self-diffusion of Mo. This strongly suggests that the rate-controlling process of the creep is governed by the bulk diffusion in Mo solid solution rather than interfacial diffusion. However, it is unlikely to be caused by Mo self-diffusion because of its lower activation energy, but it might be caused by impurity diffusion, for example, of interstitial (I)-substitutional (S) pairs. The role of Mo solid solution on ultrahigh-temperature tensile creep deformation of the MoSiBTiC alloy will be further discussed with experimental data.

2:15 PM PM06.02.03
Density Reduced Mo$_{ss}$-(Mo,V)$_3$Si-(Mo,V)$_5$SiB$_2$ Alloys <u>Julia Becker</u>[1], Ulf Betke[1] and Manja Krüger[2]; [1]Otto von Guericke University, Magdeburg, Germany; [2]IEK-2, Forschungszentrum Jülich GmbH, Jülich, Germany.

In terms of preserving resources and reducing environmental impacts, improving the efficiency of turbines for power plants and aircraft engines is an increasingly important research subject. Potential high performance materials are Mo-Si-B alloys. Consisting of a molybdenum solid solution (Mo$_{ss}$) phase and two intermetallic phases Mo_5SiB_2 (T2) and Mo_3Si those alloys present balanced room temperature fracture toughness, high temperature creep strength and oxidation performance. In this work vanadium as a lightweight element with a density of 6.1 g/cm^3 has been identified as a potential alloying partner which can entirely be solved in the Mo$_{ss}$ phase as well as in the Mo_3Si and Mo_5SiB_2 phase. To identify the role of vanadium in terms of strengthening the solid solution phase different Mo-XV (X = 5…50 at.%) alloy compositions were produced and evaluated by means of microhardness measurements. Additionally, quantitative values for solid solution hardening were determined by the approach of Labusch. Compared to other alloying concepts, e.g. Mo-Ti, vanadium affects a more balanced strength – ductility relation at room temperature, i.e. a slightly reduced strength but increased plastic deformability. In the next step, potential Mo-V-Si-B materials which provide a reduced density by about 20% as compared to reference alloy Mo-9Si-8B were investigated. Different alloy compositions were produced by powder metallurgy to observe the effects of V as a solute in the respective phases. The microstructure of the bulk Mo-40V-9Si-8B was characterized via SEM and XRD. From Rietveld refinements the preferred V sites in the lattices of the present phases were derived. The mechanical behavior was determined by microhardness measurements as well as constant displacement tests in the compressive mode between room temperature and 1100 °C. Three point-bending with notched samples as well as compressive creep tests reveal a high fracture toughness and acceptable creep strength of this new type of alloys. Therefore, the first results show a high potential as a lightweight version of Mo-Si-B alloys for structural applications.

2:30 PM PM06.02.04
A Phase Field Study on Script Lamellar Pattern of MoSi$_2$/Mo$_5$Si$_3$ Eutectic <u>Chuanqi Zhu</u>[1], Yuichiro Koizumi[2], Akihiko Chiba[1], Kyosuke Kishida[3] and Haruyuki Inui[3]; [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Department of Materials Science and Engineering, Osaka University, Osaka, Japan; [3]Center for Elements Strategy Initiative for Structure Materials (ESISM), Kyoto University, Kyoto, Japan.

MoSi$_2$-based alloys and composites have been considered as promising candidates for high temperature structural application. Directionally solidified (DS) MoSi$_2$/Mo$_5$Si$_3$ composites have a script pattern in which discontinuous Mo$_5$Si$_3$ rods inclined to the growth direction are embedded within MoSi$_2$ matrix. Since a deeper understanding of pattern formation is crucial to the microstructure design for property optimization, a phase field model based on Multiphase-Field framework has been constructed to elucidate the responsibility of continuous nucleation on solid-liquid interface for the discontinuity of this pattern, which has a close relation to material toughness. Under solidification conditions with various growth rates, three dimensional computation results of microstructures reproduced the characteristics of script pattern observed by scanning electron micrography (SEM). In addition, the simulation results show good agreement in length scale of lamellar spacing with experimental images and analytical solutions obtained by Jackson-Hunt approach.

2:45 PM PM06.02.05
Printability of Mo-Si-B Alloys via Additive Manufacturing <u>Janett Schmelzer</u>[1], Silja-Katharina Rittinghaus[2], Andreas Weisheit[2], Martin Stobik[3], Jörg Paulus[4], Karl Gruber[4], Egbert Wessel[5], Manja Krüger[5] and Christoph Heinze[6]; [1]Otto-von-Guericke-University Magdeburg, Magdeburg, Germany; [2]Fraunhofer – Institut für Lasertechnologie, Aachen, Germany; [3]NANOVAL GmbH & Co.KG, Berlin, Germany; [4]Dr. Kochanek Entwicklungsgesellschaft, Neustadt a. d. Weinstraße, Germany; [5]Institut für Energie- und Klimaforschung (IEK-2), Jülich, Germany; [6]Siemens AG, Berlin, Germany.

Current research on high temperature metallic materials focuses on Mo-Si-B alloys which are candidates for novel turbine materials. For structural applications, an important phase field in the ternary Mo-Si-B system is located between the Mo solid solution phase (Mo$_{ss}$) and the silicides Mo$_5$SiB$_2$ (T2) and Mo$_3$Si (A15), which is known as the so-called ''Berczik-triangle''. Near-eutectic Mo-Si-B alloys from this three-phase region exhibit outstanding creep properties, even above temperatures of 1100 °C, as well as a good oxidation resistance. However, ingot processing (IM) of this class of materials is challenging due to the high melting point of Mo-Si-B materials being typically > 2000 °C (eutectic Mo$_{ss}$-Mo$_3$Si-Mo$_5$SiB$_2$ alloys ~ 2000 °C). Different multi-step powder metallurgical processes (PM) were typically used in the past to produce dense Mo-Si-B samples under laboratory conditions. The introduction of a one-step processing route for this type of material via additive manufacturing (AM) or 3D printing represents an important innovation that will allow the production of complex bulk materials with net shape geometries (e.g. turbine blades). This work shows the feasibility of printing pre-alloyed near-eutectic Mo-Si-B powder materials via laser metal deposition (LMD). Therefore, Mo-Si-B powder was manufactured via gas atomization (GA) process out of solid raw materials meeting the requirements for AM regarding flowability and particle size. The specific challenge is the ultra-high melting point of this type of alloys, accompanied by problems of interlayer bonding and defects that may occur during cooling. Compact multiphase Mo$_{ss}$-Mo$_3$Si-Mo$_5$SiB$_2$ builts containing low porosity could be manufactured. For further understanding of the microstructural evolution powder particles after GA were investigated and detailed analyses of the resulting microstructure were carried out. For purpose of comparison with PM and IM Mo-Si-B alloys first

results of mechanical tests, e.g. hardness, compressive strength and creep response, are presented.

3:00 PM BREAK

3:30 PM *PM06.02.06
Room Temperature Deformation of Transition-Metal Silicides Investigated by Micropillar Compression Method <u>Kyosuke Kishida</u>[1, 2] and Haruyuki Inui[1, 2]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

Transition-metal (TM) silicides have received considerable attention as promising structural materials for ultra-high temperature applications that can replace the currently used Ni-based superalloys because of their very high melting temperature above 2000 °C, good mechanical properties and good oxidation resistance. Extensive studies using bulk single- and poly-crystals have revealed that most TM silicides can plastically deform only at high temperatures above 1000 °C. The activation of various deformation modes have been reported so far, however, some ambiguity in the identification of operative deformation modes still remains mostly because of severe oxide formation on the specimen surface as well as dislocation climb, which is inevitable in the case of high temperature experiments. Recently, the micropillar compression method first introduced by Uchic et al. has been widely recognized as a new attractive technique to investigate the mechanical response of not only pure metals but also various hard and brittle materials at size-scales of tens of micrometers or less. Recently, we have applied the micropillar compression method to single crystals of various TM silicides such as $TMSi_2$ (TM=Mo, Nb, Ta, V, Cr), TM_5Si_3 (TM=Mo, Nb, Ti) and $T2-Mo_5SiB_2$ as a function of specimen size and loading axis orientation. For most of the TM silicides tested, plastic flow was observed if the specimen size is reduced to micron meter size. For $T2-Mo_5SiB_2$ phase, three different slip systems were identified to be operative at room temperature. The values of critical resolved shear stress (CRSS) for the three slip systems in $T2-Mo_5SiB_2$ are extremely high all exceeding 2 GPa. The CRSS value for each slip system increases with the decrease in the specimen size, following the inverse power-law relationship with an exponent much smaller than those reported for FCC and BCC metals. The dissociation scheme and glide plane (actual atomic layers) of the identified dislocations in $T2-Mo_5SiB_2$ were investigated both experimentally through atomic-resolution scanning transmission electron microscopy imaging of their core structures and theoretically by first-principles calculations of the relevant generalized stacking fault energy curves.

4:00 PM PM06.02.07
Mo Base Alloys Feasibility and Optimization for the High Temperature Turbine Blades Application <u>Olha Popovych</u>[1], Hanna Tsybenko[1], Konstantin Naumenko[1] and Manja Krüger[2]; [1]Otto von Guericke University Magdeburg, Magdeburg, Germany; [2]Research Center Jülich, Jülich, Germany.

Application of the single-crystal Ni base superalloys for turbine blades at temperatures of up to 90 % of their melting point already reached the limit of their development. Because of the beneficial physical and mechanical properties at high temperatures, Mo base alloys are very promising to substitute Ni base alloys. These materials possess high temperature strength and excellent creep resistance as well as acceptable fracture toughness. Nevertheless, the replacing of Ni base superalloys in turbine applications is still a difficult problem. This study is focused on FE calculations of the deformation of a simple turbine blade made of Mo based alloys under the typical loading conditions in comparison to conventional turbine blade materials, aimed to evaluate the feasibility of Mo base alloys.
The investigations of Mo base alloys displayed the best combination of the high temperature properties for alloys containing Si and B, specifically for the alloy family with a three-phase microstructure: ductile molybdenum solid solution phase and the two intermetallic phases Mo_3Si and Mo_5SiB_2. However, an extensive knowledge about the physical and mechanical properties of each phase is not achieved, yet. In this study, the creep properties of the individual phases are determined and applied for the estimation of the creep properties of the alloy in general. This provides a possibility for the advanced alloy design.

4:15 PM PM06.02.08
Phase Field Simulation of Spontaneous $C11_b$-MoSi$_2$/D8m-Mo$_5$Si$_3$ Eutectic Reaction in Directional Solidification <u>Yuichiro Koizumi</u>[2], Chuanqi Zhu[1], Toshihiro Yamazaki[1], Akihiko Chiba[1], Koretaka Yuge[3], Kyosuke Kishida[3, 4] and Haruyuki Inui[3, 4]; [1]Tohoku University, Sendai, Japan; [2]Osaka University, Suita, Japan; [3]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [4]Center for Elements Strategy Initiative for Structure Materials (ESISM), Kyoto University, Kyoto, Japan.

$C11_b$-MoSi$_2$/ $D8_m$-Mo$_5$Si$_3$ eutectic alloys with script lamellar structure [1] have been proposed as one of the candidates for materials of next-generation gas turbine operated at extremely high temperatures above 1700 °C. The refinement of script lamellar structure and the modification the properties of lamellar interface are believed to improve the toughness at room temperature and creep resistance at high temperature, which is the key to the practical application. In this study, we have developed a phase-field model for examining the effects of various factors on the geometry of the script lamellar structure formed during directional solidification on the basis of the previously developed model for simulating lamellar structure formation in $C11_b$-MoSi$_2$/C40-NbSi$_2$ [2, 3]. The model can take into account the elastic strain energy and the relaxation of strain by structural ledges. It is also possible to include interfacial segregation of ternary elements to the model. When spontaneous decomposition from liquid to $C11_b$-phase and $D8_m$-phase was assumed, inclined lamellar structures were formed under limited conditions, and the lamellar spacing decreased with increasing cooling rate as expected. It is suggested that the nucleation of $D8_m$-Mo$_5$Si$_3$ is important for more quantitatively precise reproduction of script lamellar structure. The effects of nucleation will be presented by Zhu et al. elsewhere. Reference: [1] K. Fujiwara et al. Intermetallics 52 (2014) 72-85. [2] T. Yamazaki et al. Intermetallics 54 (2014) 232-241, [3] T. Yamazaki et al. Comp. Mat. Sci. 108 (2015) 358–366.

4:30 PM PM06.02.09
Microstructural Study of a Nb-Si Based Alloy Through the Different Steps of a Powder Metallurgy Route <u>Virgil Malard</u>[1, 2], Stefan Drawin[1], David Neumeyer[3], Jean-Philippe Monchoux[3], Anne Denquin[1] and Alain Couret[3]; [1]ONERA, Châtillon, France; [2]Paris-Saclay University, Saclay, France; [3]CEMES/CNRS, Toulouse, France.

Niobium silicide intermetallic alloys are good candidates for applications as low-pressure turbine blades in aircraft engines for service temperatures between 800°C and 1000°C. The Nb-Si based alloys are multiphase materials constituted by a niobium solid solution Nb_{ss}, silicide phases of the Nb_5Si_3-α and / or Nb_5Si_3-β (tetragonal structure) and / or Nb_5Si_3-γ (hexagonal) type, sometimes Nb_3Si type, depending on the heat treatments applied or the alloying elements added. The solidification structure is generally dendritic with more or less complex eutectic cells. Microstructure control during solidification and processing steps is essential to obtain good mechanical properties. This is difficult by conventional casting, knowing that forming processes (forging, etc.) require high temperatures for these materials which often contain more than 50 vol.% of intermetallic phases. Powder Metallurgy (PM), thanks to the microstructural homogeneity it offers, and to easier shaping processes, is a manufacturing process that deserves to be studied.

This communication reports the study of an alloy with composition 43Nb-25Ti-3Mo-3Cr-6Al-20Si (at.%). The microstructure of this alloy has been followed throughout a typical PM cycle. It is detailed for the following steps: (1) cast ingot to be atomized; (2) powders produced by inert gas atomization, of [40-100] μm and [100-200] μm particle size; (3) bulk samples obtained by Spark Plasma Sintering (SPS) at 1385°C, 1520°C and intermediate

temperatures; (4) bulk SPS samples with additional heat treatment (1500°C, 100 h). Quasi-static compression tests as well as creep tests, at 800°C and 1000°C, are presented.

The microstructures are compared with respect to the nature and morphology of the phases, the chemical homogeneity and the porosity. The main detected phases are Nb_{ss} (containing Ti, Al, Mo, Cr), two forms of the Nb_5Si_3 silicide (α or β, and γ; Nb is mainly substituted by Ti) and TiN, probably formed during ingot melting. Depending on the state of the material, the observations show, for the silicides, different sizes, chemical compositions and morphologies, as well as a variable microstructural homogeneity. The local silicon content can create hypoeutectic zones and lead to the primary solidification of Nb_{ss}. The microstructure of partially densified samples shows the sintering mechanism by Nb_{ss} diffusion at the interparticle contact points. The SPS process for niobium silicide based alloys offers good prospects for obtaining a fine and homogeneous microstructure, conferring good mechanical properties on this type of intermetallic material.

4:45 PM PM06.02.10
Characterization Crystal Phase and Thermoelectric Properties of Thin Film SrSi₂ Kodai Aoyama[1], Takao Shimizu[1], Hideto Kuramochi[2], Masami Mesuda[2], Ryo Akiike[2], Yoshisato Kimura[1] and Hiroshi Funakubo[1]; [1]School of Materials and Chemical Technology Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama , Japan; [2]Advanced Materials Research Laboratory, Tosoh Corporation, Ayase, Japan.

Silicon based alloys with good thermoelectric property such Si-Ge, Mg.Si and Mn-Si system have been widely investigated not only bulk form but also thin film form. $α$-SrSi$_2$ is also a promising candidate as a thermoelectric material because it consists of abundant nontoxic elements and a good thermoelectric power factor near the room temperature was reported by Hashimoto et al [1]. However, the number of researches is limited compared with former widely investigated silicide and there are no reports in film form. In this study, we firstly prepared $α$-SrSi$_2$ thin films on insulating substrates and measured their thermoelectric properties.
Thin films of Sr-Si system were deposited on c-Al_2O_3 substrate by using RF magnetron sputtering method at various deposition temperature and total pressure.
Constituent phases strongly depend on the deposition temperature. The films deposited below 400ºC consisted of amorphous phase. Metastable SrSi$_2$ phase with CaSi$_2$ structure was obtained between 500 and 600ºC and finally stable $α$-SrSi$_2$ above 700ºC.
Metastable SrSi$_2$ phase with CaSi$_2$ structure showed low power factor below 10 $μW/(m\,K^2)$ for the temperature range of 100-400ºC. On the other hand, $α$-SrSi$_2$ show good thermoelectric power factor beyond 700 $μW(m\,K^2)$ at room temperature. This much value is larger than observed value of Mg_2Si (111) one-axis-oriented films prepared by the same deposition process, maximum 130 $μW/(m\,K^2)$ at 300ºC. The present result shows that $α$-SrSi$_2$ is one of the promising candidates as thin film thermoelectric materials.
[1]K. Hashimoto et al., J. Appl.Phys. **102** (2017) 063703.

SESSION PM06.03: Titanium Aluminides II
Session Chairs: Svea Mayer and Sesh Tamirisakandala
Tuesday Morning, November 27, 2018
Hynes, Level 1, Room 104

8:30 AM *PM06.03.01
Productionization of Gamma Titanium Aluminides for Aerospace Applications Sesh A. Tamirisakandala; ARCONIC, Niles, Ohio, United States.

Although the benefits of titanium aluminides for high temperature applications were well conceived and significant research and development activities were conducted in the past four decades, they remained as developmental materials due to barriers associated with melting, processing, scale-up, and affordable productionization. Demanding requirements of efficient aero-engines and extensive risk reduction demonstrations paved the path for commercial introduction of gamma titanium aluminides, the single most attractive current application is for low pressure turbine blades in aero-engines replacing conventionally cast nickel superalloys. This talk provides an overview of recent progress, productionization challenges, and opportunities for improvements.

9:00 AM PM06.03.02
A Study of the Creep Properties at High Temperatures of the as-spsed IRIS-TiAl Alloy Alain Couret and Jean-Philippe Monchoux; CEMES/CNRS, Toulouse, France.

This presentation aims at describing the creep properties at high temperatures 700°C-850°C of the IRIS-TiAl alloy (Ti-48Al-2W-0.08B) densified by Spark Plasma Sintering (SPS). SPS is a technic of powder metallurgy for which the densification is due to the simultaneous application of a direct pulsed electric courant of high intensity and of a uniaxial pressure on a graphite assembly containing the powder. This process allows achieving original microstructures with enhanced properties due to its rapid processing cycle as well as non-textured, homogeneous alloys resulting from the use of the powder metallurgy route.
The as-spsed IRIS-TiAl alloy exhibits a fine microstructure made of small lamellar colonies (40 μm) which are surrounded by single phased borders made of γ grains and containing some precipitates of $β_0$ phase. Creep curves and creep results obtained between 700°C and 850°C under various stress levels will be presented. The microstructures of crept samples were studied by transmission electron microscopy. Firstly, it will be shown the activation of pure climb of [001] dislocations in (001) planes which was never reported in the literature. Secondly, the displacement mode of ordinary dislocations will be investigated with a special attention to the role of climb.
These results will be discussed to determine what is controlling the creep properties of the IRIS alloy and to explain the origin of the very high creep resistance of this alloy.

9:15 AM PM06.03.03
Microstructure Design for Enhancement of Room-Temperature Ductility in Multi-Component TiAl Alloys Ryosuke Yamagata, Yotaro Okada, Hirotoyo Nakashima and Masao Takeyama; Materials Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Japan.

TiAl alloys are required high toughness and ductility for jet-engine applications. In previous studies, we clarified that introduction of the β-Ti / γ-TiAl duplex (DP) microstructure at the α_2-Ti$_3$Al/γ lamellar colony boundaries improves the stress intensity factor range threshold ΔK and decreases the Paris exponent m. Microstructure analysis revealed many slip lines exist in γ phase in DP region. This suggested that it is possible to enhance room-temperature ductility through controlling DP microstructure. Therefore, in this study, microstructure factors to enhance room-temperature ductility was investigated in multi-component TiAl alloys.

Multi-component TiAl alloys were used in this study. The microstructure was controlled by phase transformation of $\alpha \rightarrow \beta + \gamma$ based on our phase diagram studies. Room-temperature tensile tests were conducted with a strain rate of 3×10^{-4} s^{-1} using an Instron-type universal testing machine. In order to removed surface strain that was introduced during machining, tensile test specimens were firstly electrical-polished. Microstructures observation was carried out using field-emission scanning electron microscopy.

The room-temperature ductility changes from 0.1 % to 1.4 % with increasing of volume fraction of γ phase from 5 % to 80 %. However, γ single phase alloy did not show any ductility, less than 0.1 %. Microstructure analysis revealed that the key of factors for enhancement of room-temperature ductility are the large amount of γ phase (>70%) in DP region and the existence of β phase. The other techniques and mechanisms will be discussed in presentation. This study was supported by Strategic Innovation promotion Program (SIP) in Japan.

9:30 AM PM06.03.04
Microstructural Evolution in Mo-Alloyed Al-Rich Titanium Aluminides <u>Reinhold Wartbichler</u>[1], Frank Stein[2], Martin Palm[2], Helmut Clemens[1] and Svea Mayer[1]; [1]Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria; [2]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany.

Titanium aluminides based on the intermetallic γ-TiAl phase are well-established lightweight structural materials within the temperature range from 600 to 800°C due to their high specific (creep) strength, low density and sufficient oxidation resistance. Increasing the aluminum content lowers the density even further while improving the oxidation behavior and leads to the formation of Al-rich intermetallic phases, such as r-TiAl$_2$. Although for an alloy with a given chemical composition of Ti-60at.%Al desired lamellar microstructures of γ-TiAl and r-TiAl$_2$ can be adjusted, the occurrence of metastable phases, such as h-TiAl$_2$ and Ti$_3$Al$_5$, impairs the formation of an equilibrium state and embrittles the alloy. The effects of additional alloying elements, like Mo and Nb, on the microstructural evolution of Ti-60Al are mostly unknown and were investigated in the course of this work for 1 and 3 at.% Mo, respectively, and 1 at.% Mo and 4 at.% Nb. The sample material was manufactured by vacuum arc remelting. Several heat treatments were carried out to make a proper comparison to the binary alloy system. Samples were investigated via scanning electron microscopy to visualize the evolving microstructures. X-ray diffraction was performed to identify the occurring phases. Electron probe micro analysis was executed to measure phase compositions and solubility limits. To investigate transition temperatures of stable as well as metastable phases differential thermal analysis and differential scanning calorimetry was performed. The as-cast state revealed process-related defects and cracks. Mo has segregated in all specimens during solidification, whereas Nb had not. Homogenization was possible via holding the samples at 1400°C for one hour followed by furnace cooling. Subsequently, heat treatments of 200 hours at 1000°C and 500 hours at 800°C were performed, followed by water quenching. The addition of Mo and Nb impaired the microstructural evolution and lowered the amount of r-TiAl$_2$, but lamellar structures of γ-TiAl and r-TiAl$_2$ were still obtainable in case of 1 at.% Mo. However, none of the specimens reached an equilibrium state. The range of the γ-TiAl + r-TiAl$_2$ two-phase field region decreased with increasing Mo content as well as the stability of the embrittling Ti$_3$Al$_5$-phase. Transition temperatures were determined and a quasi-binary phase diagram was generated, which visualizes the γ-stabilizing effect of Mo by increasing the range of the γ single phase field region.

9:45 AM PM06.03.05
Tribological Properties of γ-Based TiAl Alloys Under High Temperature Sliding Wear Conditions <u>Lukas Mengis</u>, Christoph Grimme and Mathias C. Galetz; DECHEMA Research Institute, Frankfurt am Main, Germany.

Due to their peerless combination of material properties at high temperatures, intermetallic titanium aluminides have already started to be implemented as a turbine blade material in the low pressure section of the turbine engine.

As turbine blades are attached to the turbine disk by a specific dovetail connection, metallic surfaces are inevitably in direct contact under harsh mechanical loads as well as thermal conditions. In this regard, friction and wear issues always occur and can strongly affect the overall lifetime of the components.

Within the scope of this study a basic analysis of the friction and wear properties of two γ–based TiAl alloys, namely TNM-B1 and GE 48-2-2, has been conducted using a high temperature pin-on-disk apparatus. Hereby, tests were performed covering a wide temperature range (up to 800°C) under variation of the counterpart material to simulate conditions that are relevant for todays turbine engines.

As oxidation plays a vital role in terms of high temperature sliding wear conditions being the decisive factor for the specific wear mechanism and rate, the basic oxidation behavior of the chosen TiAl alloys has to be additionally investigated. Isothermal exposures in air were conducted to determine the respective influence of the exposure time (up to 1000h) as well as the temperature.

Conclusively, wear losses/rates were calculated and changes in the occurring wear mechanisms were identified using a profilometer as well as different metallographic techniques to depict differences in the overall tribological performance of both substrates.

10:00 AM BREAK

10:30 AM *PM06.03.06
Accelerated Design of Gamma-TiAl Alloys by High Throughput Calculation <u>Fan Zhang</u>[1], Jun Zhu[1] and John Foltz[2]; [1]CompuTherm, Middleton, Wisconsin, United States; [2]ATI Specialty Alloys & Components, Albany, Oregon, United States.

Gamma TiAl alloys are gaining acceptance as a lighter weight alternative to nickel-based superalloys in certain high temperature applications. Further successful adoption of these alloys into new aero-engine components requires additional improvements to temperature capability and property balances. Comprehensive understanding of composition-processing-microstructure-property correlation is essential in aiding the selection of suitable alloy composition and the control of processing conditions. Although simulations tools have been developed for such a purpose, trial-and-error approaches are still widely used in alloy design and process optimization.

In this work, we will present our work in the development of a simulation tool that can be used to accelerate the design and development of gamma TiAl alloys. In particular, we developed a thermodynamic database for TiAl-based alloys using the CALPHAD (CALculation of PHAse Diagram) approach. This database contains 16 components which covers most of the major and minor alloying elements for TiAl-based alloys. We have also developed a high throughput calculation (HTC) in Pandat software through which calculations at numerous alloy compositions can be performed and alloy compositions that

satisfy user-defined criteria can be searched through data mining of the simulated results. In this presentation, we will demonstrate how we can use HTC function and the thermodynamic database we have developed for TiAl alloys to understand the effect of various alloying elements on the properties of TiAl alloys and therefore identify the alloy compositions with good potentials for certain applications.

11:00 AM PM06.03.07
Computational and Experimental Phase Diagram Study in Ti-Al-Nb-Cr Quaternary System Hirotoyo Nakashima and Masao Takeyama; School of Materials and Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Japan.

The thermodynamic modeling has been performed in order to reproduce the change in phase equilibria among β-Ti, α-Ti, α_2-Ti$_3$Al and γ-TiAl phases within the temperature range from 1573 K to 1073 K in Ti-Al-Nb-Cr quaternary system. Two ternary subsystems of Ti-Al-Nb and Ti-Al-Cr have been assessed with special attention to the α_2 stabilizing effect against α in Nb and α stabilizing effect against α_2 in Cr. Then those two systems have been combined to calculate quaternary phase diagram. In all the temperature investigated in the present study, the negative interaction exists among three elements of Al-Cr-Nb and Cr-Nb-Ti to stabilize the β against the α(α_2) and γ phases. Thus the ternary interaction parameters have been introduced and its Nb/Cr ratio, Al content and temperature dependence were optimized. The experimental validation of the thermodynamic database at the lower temperature of 1273K ~ 1073 K will be discussed both in terms of the phase transformation pathway and the change in volume fractions of the constituent phases.

11:15 AM PM06.03.08
Titanium Aluminides Under Evolution—*In Situ* and Real-Time Information Revealed by Neutron and Synchrotron X-Ray Diffraction Klaus-Dieter Liss[1, 2, 3]; [1]Guangdong Technion - Israel Institute of Technology, Shantou, China; [2]Technion – Israel Institute of Technology, Haifa, Israel; [3]MMMB, University of Wollongong, Wollongong, New South Wales, Australia.

The microstructural evolution and transformation behavior of titanium aluminides is a complex interplay in alloy design, process development and under operating conditions. In-situ neutron and synchrotron X-ray diffraction deliver unique and complementary insight into the material's response to high temperature, deformation and extreme conditions. Neutrons illuminate a larger bulk volume and reveal quantitative phase abundance, bulk texture, lattice parameter changes and other ensemble averaged quantities. In contrast, fine-bundled high-energy X-rays deliver reflections from a number of individual grains. For each constituting phase, their statistics and behavior in time reveal information about grain growth or refinement, subgrain formation, static and dynamic recovery and recrystallization, slip systems, twinning, etc. Features will be presented on selected examinations on titanium aluminides, especially to characterize phase evolution and crystallographic changes upon heating and during plastic deformation, and severe conditions.

11:30 AM PM06.03.09
Formation of Orthorhombic Intermediate Temperature Phases in Different Commercial and Experimental γ-TiAl Alloys Marcus W. Rackel[1], Heike Gabrisch[1], Uwe Lorenz[1], Andreas Stark[1] and Florian Pyczak[1, 2]; [1]Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; [2]Brandenburgisch Technische Universität Cottbus-Senftenberg, Cottbus, Germany.

γ-TiAl alloys for aero engine blades can be produced by forging but the inherent brittleness of TiAl makes this difficult. A means to facilitate forging of γ-TiAl alloys is to stabilise the ductile soft disordered β phase at forging temperature. This is achieved by the addition of β stabilising elements as for example Nb, Mo or V and was successfully implemented in the TNM alloy. In the ideal case the β phase may be present at forging temperature but can be dissolved fully at service temperature where its presence is unwanted. Unfortunately, often not only the two phases γ and α_2 are found at service temperature but additional stable or metastable phases are present. In an experimental Ti-42Al-8.5Nb alloy an orthorhombic phase constituent was identified which had the crystal structure of the O-phase and is a transformation product of α_2-phase at temperatures below 650 °C. To unambiguously identify the phase and its transformation path high-energy X-ray diffraction (HEXRD) measurements at varying temperatures using in-situ specimen environments were performed. Based on literature knowledge the occurrence of O-phase is only expected for significantly higher niobium and lower aluminum contents.
Initially it was supposed that this O-phase is a feature of this very special experimental alloy composition. Nevertheless, screening tests over a wide variety of alloy compositions proofed that the O-phase can be found in a number of commercial as well as experimental alloys depending on composition and heat treatment history. In general it can be stated that alloy compositions with a combined content of β stabilising elements of 6 at.% or more and Al contents of 46 at.% or lower form O-phase to a greater or lesser extent. Minor alloying elements, such as boron or carbon exhibited no measureable effect on O-phase formation.
The results can be valuable for the development of β stabilised TiAl alloys and the understanding of the long term behaviour of TiAl parts as the possibility of O-phase formation in the medium temperature range was until now disregarded for such alloys.

SESSION PM06.04: Titanium Aluminides III and Superalloys
Session Chairs: Alain Couret and Rui Yang
Tuesday Afternoon, November 27, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.04.01
Influence of Solidification Condition on Boride Morphology in Cast TiAl Alloys Rui Yang; Institute of Metal Research CAS, Shenyang, China.

Boron additions are indispensible in gamma TiAl alloys designed for cast applications because borides of different structures, shape, and size or their mixtures limit grain growth during solidification, subsequent solid state phase transformation, and during hot isostatic pressing. Some forms of borides, such as very long ribbons, especially when concentrated and entangled, may degrade mechanical properties. In this talk, we attempt to classify the conditions for the formation of such borides according to alloy composition, cooling rate and solidification sequence. Experimental evidence will be presented from both cast turbine blades and wedge-shape samples with step thickness. Corresponding tensile test data will be discussed.

2:00 PM PM06.04.02
Phase Equilibria among β/α_2/α/γ Phases and Phase Transformations in Ti-Al-Cr System at Elevated Temperatures Ali Shaaban[1, 2], Hideki Wakabayashi[1], Hirotoyo Nakashima[1] and Masao Takeyama[1]; [1]Department of Materials Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan; [2]Surface Protection and Corrosion Control Lab, Central Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt.

Designing of wrought TiAl alloys opens the window for a wide range of applications and it will not be exclusive to be applied as low-pressure turbine

materials but also as high-pressure compressor materials. β-Ti phase in TiAl alloys allows excellent hot workability during processing and excellent mechanical properties in service temperatures. In other words, microstructure control using β-phase is a key to develop high-toughness wrought γ TiAl alloys. This can be accomplished by understanding the phase transformations involving β-phase. Effects of group V^{th} (V, Nb) and VIth (Cr, Mo) elements as β-stabilizers on phase equilibria of TiAl alloys above 1473 K were extensively studied by our group. It was found that V and Nb stabilize α_2 against α. Also, the change in three-phase coexisting region $β+α+γ$ that exists above 1473 K to that of $β+α_2+γ$ occurs not just by the ordering transformation $α→α_2$ (2nd order phase transformation) but by a transition peritectoid reaction $β+α→α_2+γ$ (1st order phase transformation) at a temperature between 1453 K (the congruent temperature of $α→α_2$) and 1400 K (the eutectoid reaction temperature of $α→α_2+γ$) in Ti-Al binary system with decreasing temperature. Thus this phase transformation allows a unique transformation pathway for $α→α_2+β$ in the ternary systems. However, it has not been clarified yet that the addition of group VIth elements (Cr, Mo) stabilizes either α or $α_2$. Thus, in this study, the effect of Cr addition to TiAl alloy on the phase equilibria among the four phases and phase transformation pathways within the temperature range of 1473 K~1073 K were investigated using several alloys in the composition of interest. In between 1473 K-1373 K, the slope of β/α tie-line in the three-phase coexisting region of $β+α+γ$ remains basically unchanged where the Al content in β-phase is much lower than that in α-phase. However, this slope drastically rotates in a clockwise direction and the Al content between the two phases becomes nearly equal, in between 1373 K and 1273 K and below the eutectoid reaction temperature in the binary system (1400 K). This is a strong indication that thermodynamically α-phase exists even below the 1400 K, i.e. addition of Cr stabilizes α against $α_2$ and the three-phase coexisting region of $β+α_2+γ$ at lower temperatures is formed through a ternary eutectoid reaction $(α→β+α_2+γ)$ with decreasing temperature. This three-phase tie-triangle moves towards lower Al content in phase diagram. This suggests that Cr addition results in increase of the volume fraction of γ-phase with decreasing temperature even in alloys with low Al content. In between 1173 K and 1073 K, no further shift was observed in the tie-triangle meanwhile it expands towards high Cr content in β-phase. Based on these information, a novel technique for developing a new wrought γ-TiAl with excellent workability during processing at elevated temperatures and excellent toughness in service conditions, could be proposed.

2:15 PM PM06.04.03

A Dislocation-Scale Characterization of the Evolution of Deformation Microstructures on a Bulk TiAl Alloy Antoine Guitton[1, 2], Hana Kriaa[1, 2], Julien Guyon[1, 2], Emmanuel Bouzy[1, 2] and Nabila Maloufi[1, 2]; [1]Université de Lorraine – CNRS – Arts et Métiers ParisTech – LEM3, Metz, France; [2]Labex Damas - Université de Lorraine, Metz, France.

Developing new materials and understanding how they deform is the main challenge of engineers in order to follow and predict the fast evolutions of our society. For instance, in a framework of energetic cost reductions, titanium aluminide (TiAl) alloys have attracted considerable attention due to their unique combination of properties such as high specific strength and stiffness, good creep properties and resistance against oxidation and corrosion, which make them suitable candidate materials for high temperature applications [1]. However, TiAl alloys are brittle at Room Temperature (RT), *i.e.* below their brittle-to-ductile transition temperature, which lies between 800°C and 1000°C [2]. Furthermore, their complex microstructures (multiphase, different types of microstructures, specific dislocation mechanisms…) with several impacts at different scales are puzzling the materials science community. Despite intense research, literature suffers from a lack of understanding of their elementary deformation mechanisms and the precise role of microstructures [2].

In order to address these questions, we report here, an original and an innovative approach bringing the necessary information, thus allowing linking the multiscale aspects of the mechanical behavior of TiAl alloys at RT. Particularly, we bring new breakthrough on the evolution of deformation microstructures at RT in the vicinity of interfaces in γ phase of a dual-phase bulk TiAl alloy. Plastic deformation is induced locally by μN-nanoindentation. The evolution of the microstructures is characterized comprehensively by accurate Electron Channeling Contrast Imaging (aECCI) before and after deformation [3]. aECCI is a non-destructive groundbreaking procedure offering the ability to provide, inside a SEM, TEM-like diffraction contrast imaging of sub-surface defects (at a depth of about one hundred of nanometers) on centimetric bulk specimen with still unsurpassed resolutions [4]. Defects, such as dislocations, can be characterized by applying the TEM extinction criteria [5]. All features help to explain the poor ductility of the TiAl-based alloys at RT. Accommodation of the deformation is reported and a scenario is proposed [3].

References
[1] – Y. Kim, D. Dimiduk, JOM **43**, (1991).
[2] – C. Zambaldi, PhD thesis, Aachen (2010).
[3] – A. Guitton, H. Kriaa, E. Bouzy, J. Guyon, N. Maloufi, Materials **11**, 2 (2018)
[4] – H. Kriaa, A. Guitton, N. Maloufi, Scientific reports **7**, (2017).
[5] – H. Kriaa, A. Guitton, N. Maloufi, *Submitted*

2:30 PM PM06.04.04

Relationship Between the Microstructure and Atomic Relaxation Processes in the Last Generation of TiAl Intermetallics Maria L. No[1], Leire Usategui[2], Thomas Klein[3], Svea Mayer[4], Helmut Clemens[4] and Jose San Juan[2]; [1]Física Aplicada II, Universidad del Pais Vasco (UPV/EHU), Bilbao, Spain; [2]Física de la Materia Condensada, Universidad del Pais Vasco, Bilbao, Spain; [3]Materials Center Leoben, Leoben, Austria; [4]Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria.

Engineering structural intermetallics exhibit outstanding stability at high temperature. Among the different families of intermetallics, γ-TiAl alloys are good candidates for propulsion systems in aero and automotive industries. Recently a third and a fourth generation bearing Nb and Mo in well-balanced quantities and small amounts of C and Si (TNM and TNM+ alloys) have been developed. Adequate thermal treatments of these alloys give a lamellar arrangement of $α_2/γ$ colonies that exhibits a good creep resistance at high temperatures, which has been studied by tensile creep experiments and mechanical spectroscopy /1,2/. A microstructural analysis before and after the mechanical spectroscopy experiments should give important information about the mechanisms responsible for the observed behaviour and this is the approach used along this study.
In the present work two lamellar alloys were studied: Ti-43Al-4Nb-1Mo-0.1B (at%) (TNM alloy) and Ti-43Al-4Nb-1Mo-0.1B-0.3C-0.3Si (at%) (TNM⁺ alloy) with a final aging thermal treatment at 1123K and 1173K respectively. Mechanical spectroscopy measurements between 850K and 1225K show the diffusion of several solute atoms at different temperatures. The activation parameters were determined by tensile creep and mechanical spectroscopy experiments.
The regions of discontinuous precipitation surrounding the lamellar colonies were characterized by scanning electron microscopy (BSE, EDX, EBSD) technique. The lamellar $α_2/γ$ colonies and the small precipitates observed inside the lamellae were characterized by transmission electron microscopy (BF, DF, microdiffraction, nanodiffraction, STEM-HAADF, EDX) with a Titan Cubed 80-300KV working a 200KV. A good correlation between the mechanical spectroscopy results and the small precipitates characterized by TEM-STEM-EDX has been established through the corresponding models of precipitation and mechanical properties.
/1/ J. San Juan, P. Simas, T. Schmoelzer, H. Clemens, S. Mayer, M.L. Nó. Acta Mater. 65 (2014) 338-350
/2/ T. Klein, L. Usategui, B. Rashkova, M.L. Nó, J. San Juan. H. Clemens, S. Mayer. Acta Mater. 128 (2017) 440-450

facilities of SGIKER from the UPV/EHU.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

3:30 PM *PM06.04.06
The Effect of Oxidation on Microstructure and Phase Stability in the Subsurface Zone of Titanium Aluminides Exposed at High Temperatures <u>Mathias C. Galetz</u>, Anke S. Ulrich, Lukas Menigs, Alexander Donchev, Ceyhun Oskay and Diana Fähsing; DECHEMA Research Institute, Frankfurt am Main, Germany.

Titaniumaluminides had been in the focus of research for more than three decades before they finally took off as part of modern aircraft engines in 2011. Due to their density of about 4 gcm^{-3} they offer a high specific strength since they weigh only the about the half in comparison to nickel-based alloys. Thus, a favorable advantage in efficiency, noise reduction and fuel consumption is achieved. Because of their properties they gained interest also for application temperatures beyond the present range of ~750°C. This limit is defined by the strong degradation of their oxidation resistance above that temperature. Beside oxidation resistance the mechanical properties are also affect, however, the origin of this phenomenon is still under debate. In addition, several authors reported an increase in oxygen and nitrogen concentration in the surface region of TiAl-alloys. It was shown that the loss of ductility can be restored by removal of the surface and subsurface layer following high temperature exposure. One issue related to that is, that the oxygen and nitrogen uptake within the alloy are not easy accessible.
Recently developed TiAl alloys and applications such as TMB® and TMB®+ aim for even higher application temperatures and improved hotworkability. Beside γ-TiAl and α$_2$-Ti$_3$Al, such alloys additionally contain the β/β$_o$-phase, whose impact on the high temperature oxidation and mechanical properties after exposure is hardly investigated and shows the requirement of a deeper understanding of the subsurface changes in such alloys due to dissolved nitrogen and oxygen.
In this work, the impact of high temperature exposure on the subsurface microstructure of TMB as well as the resulting effect on the mechanical properties at room temperature are investigated. For the latter, 4-point bending tests are conducted on samples before and after oxidation. Oxidation tests are carried out at 900°C for varying times (24 h – 1000 h) in air. The evolution of the microstructural change (based on changes in phase fractions) in the subsurface zone is investigated over time. Based on EPMA and SEM the change of the microstructure in dependence of the distance from the surface is shown, quantified, and could be correlated to oxygen uptake. A mechanism for phase transition phenomena is proposed.

4:00 PM PM06.04.07
Microstructure—Property Relationship of Vanadium Solid Solutions, Two-Phase and Three-Phase Alloys <u>Christopher Müller</u>[1], Georg Hasemann[2] and Manja Krüger[2, 1]; [1]Institute for Materials and Joining Technology, Otto von Guericke University, Magdeburg, Germany; [2]Forschungszentrum Jülich GmbH, Jülich, Germany.

Due to the low density in combination with a high melting point, vanadium demonstrates a great lightweight potential for turbines in aircrafts or energy industry. Since vanadium as a structural material is in focus of research only recently, the effects of several alloying elements on the materials properties are not or insufficiently examined yet. Therefore, various binary V-X and ternary V-Si-X-systems, that frequently contain intermetallic phases, have been studied. By means of ingot metallurgy (arc-melting process), vanadium samples with different concentrations of alloying elements were manufactured. Resulting from this, single phase vanadium solid solutions (V$_{ss}$), two-phase and three-phase alloys were produced. Microhardness measurements and compression tests were carried out to determine the mechanical properties in dependence on the alloying components. The combination between mechanical characteristics and microstructural investigations enables conclusions concerning the materials behavior and the efficiency of solid solution strengthening and second phase strengthening. Therefore, SEM (Scanning Electron Microscopy) and XRD (X-ray Diffraction) methods were used to examine the microstructure, to identify phases and to measure elements concentration in the respective phases. Results achieved within this study may help to assess the potential of novel vanadium-based structural materials regarding to high temperature applications.

4:15 PM PM06.04.08
An Attempt to Design a New Class of Co-Based Superalloy with Improved Oxidation Resistance and Creep Property <u>Zhenghao M. Chen</u>[1], Norihiko L. Okamoto[2] and Haruyuki Inui[1]; [1]Kyoto University, Kyoto, Japan; [2]Tohoku University, Seidai, Japan.

Recently, a new ternary L1$_2$ (γ′) phase Co$_3$(Al,W), coexisting with a fcc solid-solution phase (γ) based on Co, has been discovered. With precipitation strengthening by the γ′ phase, this class of Co-base superalloy exhibits an improved high-temperature strength, compared to that of conventional Co-based superalloy. However, the creep property in ternary alloy is still insufficient, due to the insufficient high-temperature strength and the lack of γ′ in volume fraction. Besides, the oxidation resistance is also an unresolved problem. In previous studies, the effect of some alloying elements on Co-base superalloys has been investigated. Ni, Ta and Ti are effective in improving the creep property by either increasing the γ′ high-temperature strength or the γ′ volume fraction. On the other hand, Cr and Si are proved to be effective in improving oxidation resistance, but providing a negative effect on creep property, by decreasing the γ′ solvus temperature, unfortunately. Thus, in the present study, we investigate the effect of co-addition of alloying elements Ni, Ta, Ti, Cr, Si on Co-base superalloys, attempting to find out a composition exhibiting both excellent creep property and sufficient oxidation resistance, simultaneously.
Ingots of (Co$_{0.8}$, Ni$_{0.2}$)-aAl-bW-xTa-yTi-8Cr-Si (at.%; a, b, x, y≥0) were prepared by arc melting. These ingots were homogenized at 1200 ºC for 24 h in vacuum, followed by heat treatment at a sub-solvus temperature for 96 h. The γ′ solvus temperatures were determined by differential scanning calorimetry (DSC), and the microstructures were examined by scanning electron microscope (SEM). Single crystals with selected compositions exhibiting exclusive γ/γ′ two-phase cuboidal structure and reasonable γ′ solvus temperature were prepared by modified Bridgman technique, followed by heat treatment at 900 ºC for 96 h. Creep tests were performed in tension under the conditions of 137 MPa/1000 ºC and 428 MPa/900 ºC. Oxidation resistance behavior at 1000 ºC were investigated with cyclic oxidation test for 200 h (20 cycles).
Although Cr and Si alloying decrease γ′ solvus temperature drastically, substituting W (and Al) with Ta (or Ti) is an effective way to increase γ′ solvus temperature without precipitating any secondary phases (such as D0$_{19}$). Oxidation resistance in multicomponent alloys are indeed to be improved, compared to non-Cr, Si alloyed Co-7Al-8W-Ta-4Ti. However, Rupture time of tensile creep at the condition of 900 ºC /428 MPa in 4Ta and 8Ti are extremely short, only few hours. 2Ta6Ti exhibits relatively high creep property at the condition of 1000 ºC /137 MPa (103h in rupture), but still not sufficient (approximately one-third to Co-Al-8W-Ta-4Ti). It seems that, unfortunately, improving oxidation resistance and creep property simultaneously in Co-based superalloy to a utility-level may come out to be difficult, unless new type of alloying elements that increase γ′ solvus temperature more effective than Ta would be discovered.

4:30 PM PM06.04.09
Alloying of Cr-Base Alloys by Ternary and Quaternary Elements and Their Effect on Oxidation and Nitridation Resistance at High Temperatures <u>Anke S. Ulrich</u>[1], Ali Solimani[1], Petra Pfizenmaier[2], Uwe Glatzel[2] and Mathias C. Galetz[1]; [1]High Temperature Materials, DECHEMA-

Forschungsinstitut, Frankfurt a.M., Germany; [2]Lehrstuhl Metallische Werkstoffe, University Bayreuth, Bayreuth, Germany.

Due to their high melting points Cr-base alloys are future candidates for materials for high temperature applications beyond Ni-base superalloys. In addition, high Cr content alloys offer lower densities compared to the commonly used Ni-base superalloys. However, for a future successful application still an optimal alloy composition has to be defined with respect to the improvement of nitridation, oxidation, and mechanical properties at high temperatures. In this work, the influence of Si, Ge, Mo, and Pt alloying on the oxidation and nitridation resistance of Cr-rich Cr_{ss}-Cr_3Si alloys was investigated using thermogravimetric analysis at temperatures from 1050°C – 1350°C. The samples were additionally analyzed using EPMA, SEM, and XRD analysis. Based on the binary $Cr_{91}Si_9$ alloy [at.%] around 2 at.% Si were substituted by ternary elements (Ge, Mo, Pt). Before oxidation, all investigated alloys had a two phase microstructure consisting of Cr_{ss} and Cr_3Si A15 phase. During oxidation an oxide scale of Cr_2O_3 and SiO_2 formed and nitrides were found underneath the scale. However, alloying showed a significant influence on the oxide scale formation, nitridation, and oxidation kinetics. Ge substitution decreased the spallation of the oxide scale, reduced the parabolic weight gain (by oxidation and nitridation), and interestingly, also the linear weight loss induced by the formation of volatile species. In the ternary Cr-Si-X (X = alloying element) systems, Ge and Mo alloying both were enriched at the subsurface zone during oxidation and remarkably decreased nitridation and the formation of brittle Cr_2N compared to the binary Cr-Si system. Their combination in a quaternary alloy, in turn, neutralizes these positive effects. Pt acted as nitrogen getter in a ternary Cr-Si-Pt alloy by forming an antiperowskite phase which simultaneously led to increased nitrogen uptake by the sample when Pt is present at the substrate surface. In order to further optimize the alloy composition, the mechanisms of the respective elements on oxidation and nitridation behavior are proposed for the ternary and quaternary alloys.

4:45 PM PM06.04.10
A Combinatorial Study on Phase Formation and Oxidation in the Thin-Film Superalloy Subsystems Co-Al-Cr and Co-Al-Cr-W <u>Alfred Ludwig</u>[1], Dennis Naujoks[1], Martin Weiser[2], Steffen Salomon[1], Helge S. Stein[1] and Sannakaisa Virtanen[2]; [1]Institute for Materials, Ruhr-University Bochum, Bochum, Germany; [2]Materials Science, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany.

Two Co-based superalloy subsystems, Co-Al-Cr and the quasi-ternary system Co-Al-Cr-W with a constant amount of 10 at. % W, were deposited as thin-film materials libraries and analyzed in terms of phase formation an oxidation behavior at 500 °C in air. By combining energy-dispersive X-ray analysis and X-ray photoelectron spectroscopy high-throughput composition measurements, a detailed evaluation of the dependence between the initial multinary metal composition and the oxide scale composition which is forming upon oxidation on the surface of the thin film is established. Phase maps for both materials libraries are provided by high-throughput X-ray diffraction. In addition, the oxidation of a Co-Al-Cr-W bulk sample was analyzed and compared to a corresponding film in the library.

SESSION PM06.05: Poster Session
Session Chairs: Ian Baker, John Lewandowski, Seiji Miura and Soumya Nag
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

PM06.05.01
Micropillar Compression of Single Crystals of the Stoichiometric Ti₃Al and hcp-Ti <u>Kim Jingeum</u>[1], Atsushi Matsumoto[1], Kyosuke Kishida[1, 2] and Haruyuki Inui[1, 2]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials, Kyoto University, Kyoto, Japan.

Micropillar compression method has received a considerable amount of attention as a new method to investigate plastic deformation behavior of various crystalline materials in sub-micron scale. Previous studies mainly on single crystals of conventional FCC or BCC metals have revealed that various interesting features in micropillar compression experiments such as strain-burst behavior and size-dependent strength with a trend of "smaller is stronger", which is generally described with an inverse power-law relationship between the strength and specimen size. Although various models to describe the size-dependent strength have been proposed, the validity of the proposed models and their applicability to other crystalline materials with lower symmetry are still controversial. In order to understand the characteristic deformation behavior of single crystalline micropillars, systematic studies on various crystalline materials including those with lower crystal symmetry are considered to be important. In the present study, we focused on an intermetallic phase Ti₃Al with the hcp-based ordered structure of the D0₁₉ type and its parent hcp-Ti in order to investigate how the size-dependent strength varies depending on the operative deformation modes and atomic ordering. Single crystal rods of the stoichiometric Ti₃Al and hcp-Ti were grown by directional solidification using an optical floating zone furnace. Micropillar compression tests of Ti₃Al and hcp-Ti single crystals were carried out as a function of loading axis orientation and specimen size. When the loading axis is parallel to a-axis, {1-100}<11-20> prism slip was confirmed to be activated in micropillars of both Ti₃Al and hcp-Ti. The values of critical resolved shear stress (CRSS) of the prism slip for both Ti₃Al and hcp-Ti were higher than those obtained for bulk single crystals. The CRSS value of the prism slip for each material exhibited a "smaller-is-stronger" trend approximately following an inverse power-law relationship. The power-law exponent for Ti₃Al was found to be much lower than that of hcp-Ti. Possible influences of the ordered structure on the difference in the size-dependent strength for the prism slip will be discussed based on the TEM observations of dislocations.

PM06.05.02
High-Resolution Electron Transmission Microscopy Study of Orthorhombic Phase in High Nb-Containing Lamellar γ-TiAl Alloy <u>Jian Sun</u>; Shanghai Jiaotong University, Shanghai, China.

Recently, the formation of nano-scale modulated microstructure, consisting of orthorhombic phase and α_2 has been reported by several authors in high Nb-containing lamellar γ-TiAl alloys. However, the occurrence of such a unique modulated microstructure in high Nb-containing lamellar γ-TiAl alloys cannot be expected from the Al-Nb-Ti ternary phase diagram in the literature. Moreover, the formation mechanism and evolution of the modulated microstructure in high Nb-containing lamellar γ-TiAl alloys remain unclear and need to be investigated.

In this work, we have proved that the orthorhombic phase is thermodynamically stable in the α_2 phase in high Nb-containing γ-TiAl alloys at high temperatures from the first-principles calculations. Transmission electron microscopy (TEM) studies showed that the formation of modulated microstructure takes place at temperature at and below 650 °C. The orthorhombic phase as a constituent of the modulated structure has the O1 structure with a random occupancy of Ti and Nb atoms on the Wyckoff sites 8g and 4c2. The O1 phase has a thin plate-like morphology with orientation relationships of $\{001\}_O//\{0001\}_{\alpha_2}$ and $<110>_O//<110>_{\alpha_2}$ at an initial precipitating stage. The habit plane for the O1 phase lies at $\{350\}_O//\{130\}_{\alpha_2}$. TEM results further exhibited a remarkable enrichment of Nb in O1 phase, indicating that the formation of the O1 phase arises from a phase separation reaction

in the α_2 matrix, dominated by a diffusion mechanism. With an extension of annealing time up to 500 hours at 600 °C, the volume fraction of the O1 phase increases remarkably, and the O1 variants interact with each other and eventually develop into rectangle shape with perpendicular interfaces from the thin plate-like morphology. The retransformed α_2 phase at intersection points has been found to rotate by ~3.4 ° to the original α_2, leading to the formation of orthogonal habit planes for the single O1 variant. The nano-indentation tests showed that the precipitation hardening effect of the O1 phase is significant in high Nb-containing lamellar γ-TiAl alloys.

PM06.05.03
Ordering and Disordering of β Phase in TiAl Alloys in Dependence of Alloy Composition <u>Victoria Kononikhina</u>[1], Andreas Stark[1], Weimin Gan[1], Andreas Schreyer[2] and Florian Pyczak[1]; [1]Helmholtz-Zentrum Geesthacht, Geesthacht, Germany; [2]European Spallation Source ERIC, Lund, Sweden.

γ-TiAl based alloys recently have started to replace Ni-based superalloys as a material for turbine blades in the low pressure turbine section of aircraft engines. γ-TiAl based alloys are characterized by low density (4 g per cm^3), good oxidation and corrosion resistance, and high specific tensile and creep strength. The presence of the γ and α_2 lamellar colonies is desirable for good mechanical properties. Cubic phase being in its disordered state (A2 structure) improves the forging properties of the alloys due to its high plasticity. The presence of ordered β_o phase (B2 structure) on the other site should be prevented because it increases the alloys brittleness at the working temperatures of about 700-800°C and has bad creep strength. Therefore, knowledge about the presence of β phase and of its ordering/disordering temperature is of high importance for the development of alloys with improved processing properties and for a prolongation of the turbine blades working time. Currently the presence of ordered β_o phase in the binary phase diagram is still under discussion and the influence of the different β stabilizing elements on the ordering/disordering temperature is not systematically investigated.
We studied the ordering/disordering transformation with *in-situ* synchrotron and neutron diffraction techniques. A good contrast of neutron diffraction between ordered and disordered β_o/β was used to confidently determine the presence of ordered β_o. Three binary TiAl alloys (Ti-xAl with x = 39, 42 and 45) and five alloys with additional alloying elements (Ti-42Al-2Y with Y = Nb, Mo, Ta, Cr and Fe) were investigated. Three ternary alloys with 2 at. % of Fe, Cr, and Mo contain correspondingly 12, 8, and 18 vol.% of the ordered β_o phase. By synchrotron investigations we determined the degree of ordering via both site occupancy calculations and correlation between superstructural and fundamental reflections for a and b phases. Alloys with 2 at.% of Cr and of Fe have degrees of ordering of about 65% and with Mo of about 58%. The evolution of the phase composition during the experiments was calculated by Rietveld refinement using the MAUD programm.

PM06.05.04
***In Situ* SEM Observation and Measurement of Strain Localization During Tensile in γ-TiAl Based Alloys** <u>Yotaro Okada</u>[1], Loris J. Signori[2], Ryosuke Yamagata[1], Hirotoyo Nakashima[1] and Masao Takeyama[1]; [1]Materials Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Japan; [2]Metallurgy and Ceramics Science, Tokyo Institute of Technology, Meguro-ku, Japan.

γ-TiAl based alloys are promising materials for high temperature applications up to 800°C because of their light weight and high creep strength. However, the application of this material to jet engines is limited to the last stages of low pressure turbine blades due to low ductility and toughness for now. In order to apply this material to other parts such as high pressure compressor, toughening is essential. We performed fatigue crack growth tests on wrought TiAl alloys and revealed that introduction of β-Ti/γ duplex (DP) along α_2-Ti$_3$Al/γ lamellar colony boundaries increased the fatigue threshold, ΔK_{th} and decreased the Paris exponent, *m*. We proposed that the improvement of ΔK_{th} is partly caused by the deformation of the DP microstructure. In order to verify this proposed mechanism, the quantification of deformation in each phase is important. In the present study, *in-situ* observation of tensile deformation in TiAl based alloys under an SEM at room and high temperatures is performed, and strain localization is measured by digital image correlation (DIC) technique. Three dimensional observation of the un-deformed and deformed materials is also conducted to observe the morphology of the microstructure and the crack stop points. The alloy with nearly lamellar (NL) microstructure, in which the volume fraction of DP is 7%, shows elongation of 0.14% at room temperature. Deformation is observed in both lamellar colonies and DP region in NL microstructure as a result of the strain localization measurement by DIC technique. In some favorably oriented lamellar colonies, strain localization along lamellae is more than five times as much as the macroscopic strain. The amount of deformation in each phase and the crack initiation and growth behavior during tensile will be discussed. This study was supported by Strategic Innovation promotion Program (SIP) in Japan.

PM06.05.05
Effects of Ta and Nb Addition on the Microstructure and Mechanical Properties of MoSi$_2$/Mo$_5$Si$_3$/Mo$_5$Si$_3$C Eutectic Composites <u>Kosei Takeda</u>[1], Yuki Kambara[1], Hirokata Matunoshita[1], Kyosuke Kishida[1, 2] and Haruyuki Inui[1,2]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

MoSi$_2$ with the tetragonal C11$_b$ structure has been considered as a promising material for ultra-high temperature structural applications because of its high melting point (2020 °C), excellent oxidation resistance, and relatively low density. However, poor fracture toughness at room temperature and insufficient high-temperature strength are still drawbacks to be improved for its practical applications. One possible way to solve these drawbacks is to form an in-situ composite with one or two strengthening phases. *Among various candidates, we have recently focused on* MoSi$_2$/Mo$_5$Si$_3$ eutectic composites because of their high eutectic temperature (1900 °C for the binary alloy) and fine microstructures of the so-called script lamellar type formed simply by directional solidification (DS) and have studied the influences of ternary additions on the microstructure and mechanical properties of DS MoSi$_2$/Mo$_5$Si$_3$ eutectic composites. Our previous studies have revealed that their high-temperature mechanical properties and fracture toughness values can be improved through refining the lamellar structure and controlling interfacial properties such as interfacial segregation of ternary elements and lattice misfits. We also have found that the DS ternary alloys with a small addition of C possess a homogeneous three-phase script lamellar structure composed of MoSi$_2$, Mo$_5$Si$_3$, and Mo$_5$Si$_3$C and exhibit higher yield strength than the binary two-phase counterpart. In the present study, effects of Ta and Nb addition on the microstructure and mechanical properties of MoSi$_2$/Mo$_5$Si$_3$/Mo$_5$Si$_3$C eutectic composites were investigated in order to establish a way to further improve the mechanical properties of MoSi$_2$/Mo$_5$Si$_3$–based eutectic composites. When part of Mo was substituted with Ta or Nb, a relatively homogeneous three-phase eutectic lamellar structure was obtained only at growth rates lower than 10mm/h during the DS process using an optical floating zone furnace, while a heterogeneous eutectic microstructure with a cellular morphology was developed at higher growth rates. Nb atoms were partitioned mostly into Mo$_5$Si$_3$C, while Ta atoms were partitioned into both Mo$_5$Si$_3$ and Mo$_5$Si$_3$C. Both volume fraction and average thickness of MoSi$_2$ lamellae decreased in the Nb alloyed eutectic composites compared to those in the non-alloyed counterpart, which resulted in higher yield strength and better creep property of the Nb alloyed eutectic composites.

PM06.05.06
Phase Diagrams and Solidification Paths of MoSiBTiC Alloys <u>Ryogo Sawada</u>[1], Makoto Ohtsuka[1], Haruki Nakashima[1], Kyosuke Yoshimi[2] and Hiroyuki Fukuyama[1]; [1]IMRAM, Tohoku University, Sendai, Japan; [2]Graduate School of Engineering, Tohoku University, Sendai, Japan.

MoSiBTiC alloys are expected to be used for next generation high-pressure turbine blades. However, the phase diagrams of the alloys are still deficient. Our group has developed an ultra-high-temperature thermal analysis using blackbody radiation, which can be used above 2000 °C. In this study,

MoSiBTiC alloys with several different compositions were thermally analyzed with this equipment to evaluate their phase transformation temperatures. In addition, the alloys were levitated and melted by electromagnetic levitation (EML) technique in a static magnetic field to observe solidification phenomena, and to obtain rapidly-solidified sample. The solidification paths of the alloys were studied from the thermal analysis and microstructures, and the partial phase diagrams of the alloys were constructed.

Each alloy powder was filled in a CaO-stabilized ZrO_2 crucible having a blackbody cavity, and then heated and cooled in a radio-frequency furnace under Ar atmosphere. The heating and cooling rates were fixed at 10 °C / min. The sample was kept above 2000 °C for over 30 min to ensure homogeneous melt, and then cooled. Temperature change during cooling was measured by a pyrometer, through the radiance from the blackbody cavity. The phase transformation temperatures were obtained from the cooling curves. On the other hand, each alloy was levitated and melted by EML technique in a static magnetic field of 10 T. The static magnetic field was applied to suppress convection in the melts. The temperature of the melts were measured by a pyrometer and controlled by adjusting the power of a heating laser. Multi-recalescence was observed at the surface of the alloys during cooling. The levitated alloys were held at the temperature just after each recalescence for about 10 min and rapidly cooled by blowing He gas to freeze the high-temperature structure. The cross-sectional microstructures of rapidly-solidified alloys were observed by a scanning electron microscope.

As an example, results of Mo-5.0Si-10.0B-8.8Ti-8.8C (mol%) alloy were described as follows; five inflection points appeared on the cooling curve during thermal analysis of this alloy. From the microstructure analysis, the following solidification path was proposed. The first point corresponds to the liquidus temperature, at which the Mo solid solution (Mo_{ss}) phase begins to precipitate as a primary phase. Subsequently, the Mo_2B phase precipitates from the melt, and the (Mo_{ss}-TiC) eutectic reaction takes place, which is followed by the (Mo_{ss}-T_2-TiC) eutectic reaction. Finally, the (Mo_{ss}-T_2-Mo_2C) eutectic reaction occurred, and the solidification completes below 1800 °C. Thus, utilizing combination of the ultra-high-temperature thermal analysis technique with the EML technique revealed the complicated solidification path of MoSiBTiC alloys. Other compositions of the alloy were similarly studied, and the partial phase diagrams of the alloys were constructed. The details will be presented in the conference.

PM06.05.07
Phase Equilibrium and Mechanical Properties of Cr-Mo-Nb-Si-B Alloys Composed of BCC and T₂-silicide Phase <u>Daisuke Goto</u>[1], Ken-ichi Ikeda[2] and Seiji Miura[2]; [1]Department of Materials Science and Engineering, Hokkaido University, Sapporo, Japan; [2]Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan.

For improving energy efficiency a new class of high temperature materials based on refractory elements have been investigated. It was already reported that the alloys based on Nb and Mo are composed of BCC solid solution (Nb-Mo) and T_2-silicide $(Nb,Mo)_5(Si,B)_3$. Further investigation on alloy phase equilibrium are needed for improved mechanical properties and oxidation resistance.

Cr is one of the candidate to modify the properties of the alloy because Cr is expected to stabilize T_2 compound phase with B. In the present study the phase equilibrium among BCC solid solution and T_2 compound are widely investigated in Cr-Mo-Nb-Si-B system. Alloys are prepared using an Ar-arc melting machine and heat-treated at 1400 ºC for 168 h. Microstructures are investigated using FE-SEM (JEOL, JXA-8530F). Constituent phases are identified using XRD (PHILIPS, X'Pert Pro), FE-EPMA (JEOL, JXA-8530F) and AES (Auger Electron Spectroscopy, JEOL, JAMP-9500F).

In the Cr-Mo-Nb-Si-B system BCC-T_2 two-phase microstructure are found in Mo-rich alloys. B/Si ratio in T_2 phase increases with increasing Cr, while almost no B solubility was found in BCC solid solution. With increasing Si in alloys, A15 silicide phase $((Cr, Mo, Nb)_3Si)$ and/or Laves phase are stabilized.

This work was supported by the Advanced Low Carbon Technology R&D (ALCA) program of the Japan Science and Technology Agency (JST).

PM06.05.08
High-Temperature Oxidation Behavior of a Ti₅Si₃-Containing Multiphase MoSiBTiC Alloy <u>Xi Nan</u>, Mi Zhao and Kyosuke Yoshimi; Tohoku University, Sendai, Japan.

The 1st-generation MoSiBTiC alloy (65Mo-5Si-10B-10TiC, mol.%) has great potential in high temperature structure application because of its comparable density with Ni-based superalloys (~8.8 g/cm³) and excellent high-temperature strength. However, its poor oxidation resistance, especially at intermediate temperatures (700-900°C) prevents them from practical uses. A recent work by Zhao et al. showed that the introduction of Ti_5Si_3 into MoSiBTiC alloy was able to improve the oxidation resistance, but without detailed oxidation mechanisms provided. In this study, the oxidation behavior of a Ti_5Si_3-containing MoSiBTiC alloy is systematically investigated at various temperatures, aiming to clarify the effect of Ti_5Si_3. The alloy was prepared by arc-melting and then annealed at 1700°C for 24 hours. Oxidation tests were carried out in a thermo-gravimetric analyzer (TGA) for different time periods. Microstructures before and after oxidation tests were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The heat-treated 38Mo-20Ti-17Si-5B-10TiC alloy was composed of Mo_{ss}, Mo_3Si, Mo_5SiB_2, Ti_5Si_3 and TiC phases. During oxidation test at 700°C, the alloy exhibited an initial transient stage of weight gain followed by a steady state of weight loss. An initial transient stage, a steady stage and an acceleration stage leading to catastrophic failure were observed at 800°C. The oxidation kinetic curves obtained at 900-1200°C showed continuous weight loss, including an initial transient stage and a steady state.

PM06.05.09
Topological Approach to Quantification of Microstructure in Mo-Si-B-TiC Alloys and Their Fracture Toughness <u>Sojiro Uemura</u>[1], Takateru Yamamuro[2], Kyosuke Yoshimi[3] and Sadahiro Tsurekawa[4]; [1]Department of Materials Science and Engineering, Kumamoto University, Kumamoto, Japan; [2]Technical Division, Kumamoto University, Kumamoto, Japan; [3]Department of Materials Science, Tohoku University, Sendai, Japan; [4]Division of Materials Science and Chemistry, Kumamoto University, Kumamoto, Japan.

Mo-Si-B-TiC alloys are expected as a candidate for ultrahigh-temperature materials to replace Ni-base superalloys, because they have a low density, a superior high-temperature strength and a high fracture toughness. The alloys have complicated microstructures consisting of molybdenum solid solution (Mo_{ss}), Mo_5SiB_2 (T_2), $(Ti, Mo)C_x$ and $(Mo, Ti)_2C$ phases and their eutectic phases. However, it has been still unclear how the microstructure affects mechanical properties of these alloys. It was reported that the topology like fractal analysis and percolation analysis were useful to correlate the microstructure with mechanical properties such as intergranular fracture. Accordingly, we applied the topological approach to evaluate microstructure in Mo-Si-B-TiC alloys and examined the correlation between topological parameters and the fracture toughness.

Four distinct Mo-Si-B-TiC alloy ingots with the same composition (65Mo-5Si-10B-10TiC (at%)) were produced via conventional arc-melting (20g and 90g), drop-casting and plasma arc-melting techniques in an Ar atmosphere, followed by heat-treatment at 2073 K for 24 hours. Microstructure in those samples was observed by SEM, and then percolation and fractal analyses were performed on the binarized SEM-BSE images. The EPMA was used to evaluate the chemical composition of constituent phases. The fracture toughness, K_Q, was evaluated using a three-point bending test based on the Irwin's similarity relationship [1]. Three-points bending tests were conducted at a displacement rate of 5 μm/s. The specimens with the Chevron-notch had final dimensions of 2.5 mm (w)×2.5 mm (h)×12.5 mm (l). The Chevron-notches were machined by electro-discharge machining with a brass wire of 0.1 mm in diameter.

The SEM observation and EPMA analysis revealed that the area fraction of constituent phases and their compositions in those Mo-Si-B-TiC alloys were almost the same, but microstructures were different. The percolation probability of hard phases: Mo_5SiB_2, $(Ti, Mo)C_x$ and $(Mo, Ti)_2C$, was found to be more than 85%, whereas that of Mo_{ss} was less than 20%. Accordingly, the microstructural feature of those alloys that the Mo_{ss} clusters were distributed

around the continuous hard phases, and then the fractal dimension of dispersion [2] of Mo_{ss} phase was determined. The fracture-toughness of those alloys were measured to be in the range of 14.6~15.6 MPa (m) $^{1/2}$. There appeared no clear relation between the fractal dimension of dispersion [2] for Mo_{ss} clusters and the fracture-toughness of those alloys. However, of particular importance is finding that the fracture-toughness monotonously increased with increasing a new parameter that was multiplied the fractal dimension of dispersion by the average perimeter of Mo_{ss} clusters.

[1]T. Moriyama, K. Yoshimi, M. Zhao, T. Masnou, T. Yokoyama, J. Nakamura, H. Katsui, T. Goto: Intermetallics **84** (2017) 92-102.
[2]Y. Mizuno, K. Terashita and K. Miyanami: *Kagaku Kogaku Ronbunshu* **19**-1 (1993) 21-29.

PM06.05.10
Oxidation Resistance and High-Temperature Strength of Cr-Added Novel MoSiBTiC Alloy <u>Tomotaka Hatakeyama</u> and Kyosuke Yoshimi; Tohoku University, Sendai, Japan.

1st generation MoSiBTiC alloy, which mainly consists of Mo_{ss}, $Mo_5SiB_2(T_2)$ and TiC phase, is expected to be a possible candidate for novel ultra-high temperature material because of its outstanding mechanical properties. However, its insufficient oxidation resistance at elevated temperature has caused barriers in practical application.
In this study, we attempted to improve the oxidation resistance by two steps. First, by increasing Si with Ti content, a Mo_{ss}-T_2-Ti_5Si_3-TiC four-phase alloy was developed. The introduction of Ti_5Si_3 phase is aimed to increase a Si resource in the microstructure. Second, Cr was added on the four-phase alloy to reinforce its oxidation resistance especially at intermediate temperature around 800°C. The Cr addition maintains the constituent phases of the alloy in a compositional range, and thus a Cr-added four-phase MoSiBTiC alloy was successfully developed at a composition of Mo-10Cr-28Ti-14Si-6C-6B (mol%). As expected, newly developed MoSiBTiC alloy exhibited a much better oxidation resistance at 800°C than 1st generation one. The alloy composition modification led to the formation of protective Cr oxide below an outermost Ti oxide layer. In addition, this alloy has a much smaller density of about 7.1 g/cm^3, resulting in about 20% improvement in the high-temperature specific strength at 1400°C compared with that of 1st generation alloy.

PM06.05.11
Variation in Positive Temperature Dependence of Strength of $L1_2$ Intermetallic Compounds in $Co_3(Al,W)$-Co_3Ti Pseudo Binary System <u>Mikio Oomae</u>, Takeshi Teramoto and Katsushi Tanaka; Kobe University, Kobe, Japan.

The influence of composition in $Co_3(Al, W)$-Co_3Ti pseudo binary system on the positive temperature dependence of strength of the $L1_2$ intermetallic compound has been examined. Some $L1_2$ ordered pseudo binary alloys were prepared and those 0.2% flow stresses were determined by a compression test from room temperature to 1273 K. The pseudo binary alloys show the intermediate onset temperature of the anomalous yield stress between the component alloys of $Co_3(Al, W)$ and Co_3Ti. Since the onset temperature is closely related to the thermally activated cross-slip from {111} glide plane to the {010} non-glide plane known as the Kear-Wilsdorf (KW) locking mechanism. The values of the activation energy and of the pre-exponential factor were derived from an Arrhenius-type plot of the increase in the 0.2% flow stress. On the simple assumption where the values of the activation energy and of the pre-exponential term in a pseudo binary alloy have a linear relationship with its composition, the experimentally determined temperature dependence of 0.2% flow stress are roughly represented, though the calculated values of the activation energy and of the pre-exponential term are slightly different to those experimentally determined.

PM06.05.12
Effect of Ni, Ta Alloying on Yield Stress Anomaly in $Co_3(Al,W)$ Strengthening Phase with $L1_2$ Structure <u>Zhenghao M. Chen</u>[1], Norihiko L. Okamoto[2] and Haruyuki Inui[1]; [1]Kyoto University, Kyoto, Japan; [2]Tohoku University, Sendai, Japan.

Recently, a new ternary $L1_2$ (γ′) phase $Co_3(Al,W)$, which can coexist with a fcc solid-solution phase (γ) based on Co, has been discovered. We have investigated the compression deformation behavior in polycrystals of the $L1_2$-$Co_3(Al,W)$ and found that $Co_3(Al,W)$ exhibits a positive yield stress-temperature dependence (yield stress anomaly: YSA) as in the case of Ni_3Al and many other $L1_2$ compounds. However, our previous study of micropillar single crystals of $L1_2$-$Co_3(Al,W)$ has demonstrated that, the high-temperature strength of $Co_3(Al,W)$ is considerably lower than that of Ni_3Al-based $L1_2$ compounds, due to a narrow temperature range of YSA in $Co_3(Al,W)$ (950-1,100 K). Another study indicates that complex stacking fault (CSF) energy as well as γ' solvus temperature might be the key of improving the high-temperature strength of $Co_3(Al,W)$.
In the present study, we investigate the effect of Ni, Ta alloying on the anomalous temperature range in $Co_3(Al,W)$. Compression tests were conducted from 298 to 1,423 K in vacuum. The onset as well as peak temperatures of YSA were thus determined from yield strength-temperature curves. Dislocations in specimen deformed at high temperatures were investigated with TEM. While, γ' solvus temperature was determined by differential scanning calorimeter (DSC). Slip trace formed at high temperatures was investigated by scanning electron microscopy with electro back-scatter diffraction.
The result indicates that, with Ni, Ta alloying, reported to be effective to increase the CSF energy, the onset temperature of YSA shifts to the low temperature side. TEM observation reveals that dislocations introduced above onset temperature exhibit strong tendency to along in its screw orientation while that below onset temperature are curved and no special orientation preferred, indicating that YSA in alloyed $Co_3(Al,W)$ is also corresponding to the K-W lock. Thus, it is evident that alloying increasing CSF energy is effective in widening the YSA region by shifting onset temperature to the low temperature side. On the other hand, alloyed $Co_3(Al,W)$, possessing higher γ' solvus temperature, exhibits also higher peak temperature, compared to ternary $Co_3(Al,W)$. However, the correspondence between peak temperature and γ' solvus temperature is not so strong among the alloyed $Co_3(Al,W)$, indicating that other effects, such as diffusing, may also influence on the mechanical properties at high temperature. Nevertheless, the slip trace analyses indicates that (111) slip takes place exclusively above the temperature range and no slip plane transition occurs in the vicinity of peak temperature, unlike Ni_3Al, in which the peak temperature corresponds to the (111)=(001) transition.
We confirmed that CSF energy is a dominant parameter of determining the onset temperature of YSA in both ternary and alloyed $Co_3(Al,W)$. On the other hand, γ' solvus temperature is a very important parameter, although may not be the only one, on peak temperature.

PM06.05.13
Effect of Multi-Elements Substitution on the Mechanical Properties of Intermetallic Compound <u>Syuki Yamanaka</u>[1], Ken-ichi Ikeda[2] and Seiji Miura[2]; [1]Department of Materials Science and Engineering, Hokkaido University, Sapporo, Japan; [2]Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan.

It is well known that various elements substitute for a certain sub-lattice of intermetallic compounds. There are various experimental investigations on the effect of substitution elements on the mechanical properties, however, there are few reports on the effect of multi-elements substitution. In the present study, $L1_2$ type compound Ni_3Al is selected as a model compound because its substitution behavior is established. It was reported that various elements such as Co, Cu, Pd and Pt substitute for Ni-site, while Si, Ga, Ge, Ti, V, Nb, Ta, Mo, W substitute for Al-site. These elements are expected to introduce local lattice distortion which may have effects on the motion of dislocations not only at room temperature but also at lower temperature region or higher temperature region. Several alloys composed of 5 or more elements including Ni, Co, Al, Mo, W are prepared using Ar-arc melting machine and heat-treated at 900 ºC for 168 h. Microstructures are investigated using FE-SEM (JEOL, JXA-8530F). Constituent phases are identified using XRD (PHILIPS, X'Pert Pro) and FE-EPMA (JEOL, JXA-8530F). Mechanical properties of phases are investigated using nano-indenter (Hysitron, TI-950 Triboindenter)

with a load of 10000 micro-N. Several alloys are found to include (Ni, Co)$_3$(Al, Mo, W, …) - L1$_2$compound as one of the constituent phases. The hardness of these L1$_2$phase investigated using nano-indenter are almost the same or higher than that of high strength Co$_3$(Al,W) -L1$_2$ compound, and it is confirmed that multi-elements substitution is an effective way to improve mechanical properties of Intermetallic compound.

PM06.05.14
Effect of Ta Addition on Microstructure and Mechanical Properties of Dual Two-Phase Ni$_3$Al-Ni$_3$V Intermetallic Alloy Kazushige Ioroi, Yasuyuki Kaneno and Takayuki Takasugi; Osaka Prefecture University, Sakai, Japan.

A dual two-phase intermetallic alloy exhibits microstructure composed of primary Ni$_3$Al (L1$_2$) phase surrounded by a eutectoid microstructure comprised of Ni$_3$Al and Ni$_3$V (D0$_{22}$) phases which is formed by a eutectoid reaction from A1 (fcc) phase. The intermetallic alloy with the dual two-phase microstructure shows attractive mechanical properties as high-temperature structural materials [1]. However, further increasing in mechanical properties is required to be used as advanced high-temperature structural materials. It has been reported that Ti and Nb not only stabilize the two constituent phases [2] but also play a role in effective solid solution strengtheners [3]. In this study, the effect of Ta addition which is other potential solid solution strengthener in the dual two-phase intermetallic alloy is investigated. Ta was added to a base alloy with a composition 75Ni10Al15V (in at.%)+50 wt.ppm B by three substitution methods for Ni, Al and V. Alloy button ingots prepared by arc-melting were solution-treated at 1553K for 5 h in a vacuum, followed by furnace cooling at a rate of 10 K/min. Microstructure observation was carried out by scanning electron microscopy (SEM) and electron probe micro analyzer (EPMA). Lattice parameters of the constituent phases were calculated from X-ray diffraction (XRD). Mechanical properties were evaluated by Vickers hardness test at room temperature.
The dual two-phase microstructure was especially fine in the 2Ta(Al) alloy among three substitution methods where the alphabet between the parentheses indicates the constituent element substituted by Ta. The hardness was observed to be ranked in order, the Base < 2Ta(V) < 2Ta(Ni) < 2Ta(Al) alloys. The solid solution hardening predicted from the unit cell volume increment rate $|dV/dC|$, where V is unit cell volume and C is Ta content dissolving in the constituent phases, is ranked in order, Ta(Al) ~ Ta(V) < Ta(Ni). Based on the observed results of microstructure and hardness, and the calculation on lattice expansion in the constituent phases, it is suggested that the additional hardening operating on the 2Ta(V) and 2Ta(Ni) alloys is dominated by the solid solution hardening while that operating on the 2Ta(Al) alloy is dominated by the hardening due to fine microstructure in addition to the solid solution hardening, consequently resulting in the largest hardness.

[1] Y. Nunomura, Y. Kaneno, H. Tsuda and T. Takasugi, Acta Materialia, 54 (2006) 851-860.
[2] S. Kobayashi, K. Sato, E. Hayashi, T. Osaka, T.J. Konno, Y. Kaneno, T. Takasugi, Intermetallics, 23 (2012) 68-75.
[3] K. Kawahara, T. Moronaga, Y. Kaneno, A. Kakitsuji and T. Takasugi, Materials Transaction, 51 (2010) 1395-1403.

PM06.05.15
A New ni-Based Superalloy for Parts of Advanced Engineering Plastics Injection Molding Machines Takahiro Nakano, Hiroshi Nakamoto and Nobuyuki Funahira; Nachi-Fujikoshi Corp., Toyama-shi, Japan.

Use of engineering plastics has been steadily increasing in advanced industry hardware; automobiles, trains, aerospace, electronic parts, and electricity production/storage, which always demand materials with lighter, stronger, and more heat resistant properties, which has been persistent to attain their better performances, as called "high performance plastics". A recent example is a group of fluorocarbon polymers (PFA) gradually replacing currently popular engineering thermoplastics or metals. PFA, however, stays elastic at low temperatures and shows its plasticity only above a transition temperature (>400 °C). Engineering plastics have been made into many product shapes of complex geometries through injection molding machines with critical parts made of many conventional tool (high strength, high carbon) steels. However, for advanced engineering plastics, like PFA, we need wrought metals with more heat resistant strength. Another inevitable property required for those parts is resistance against hot corrosion, as those parts' surfaces are continuously exposed to high temperature corrosive gas during the PFA plasticization process. In this study we developed a new Ni-based wrought superalloy, (hereinafter called "F-alloy") to be used for critical parts of advanced engineering plastics injection molding machines.
F-alloy has a characteristic as follows; the composition of this alloy was determined according to the L18 table of the design of experiment(DOE), which commonly practiced by a quality engineering method and enabled us to not only reduce a number of experiments for new alloy developments but grasp quantitatively influence of each elements to the target properties; hardness and corrosion-resistance to PFA.
Experiment procedure is as follows; 18 melts of ingots, 10kg each, with 18 different composition were made by a laboratory induction melting furnace. The major alloy elements and composition were selected according to the L18 table of "DOE" . The mechanical and metallurgical test samples were machined out from bars and plates made through press forging the 18 ingots, followed by heat treatments (solution and aging) at the temperatures predetermined by thermal and metallurgical analyses.
Hardness of F-alloy was measured at room temperature up to at 900 °C and the results were compared to the data of a conventional corrosion-resistant alloy (UNS N10276), a tool steel (UNS T30402), which has been commonly used for the parts of present injection molding machines. Hot corrosion tests were performed for F-alloy and two reference materials, the said corrosion-resistant alloy, and the said tool steel, being exposed to an environment composed with PFA at 400 °C .
The results of those experiments show that this alloy has both hardness (Hv600 at 400 °C) and good hot corrosion-resistance to PFA at 400 °C , which is an outstanding characteristic compared to conventional materials for the parts of PFA injection molding machines.

PM06.05.16
Crystallographic Anisotropy of FeCr Sigma Phase (*tP*30) Caused from Site Occupation Behaviors in Fe-Cr-M Ternary Systems Souta Maruyama, Satoru Kobayashi and Masao Takeyama; Materials Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan.

To clarify the nature of FeCr-σ phase (*tP*30), the structural features of σ phase in Fe-Cr binary and Fe-Cr-M ternary systems were investigated in this study. All of the alloys have a composition of (Fe$_{50}$)(Cr$_{50-X}$, M$_X$), (Fe$_{50-X}$, M$_X$)(Cr$_{50}$) or (Fe$_{50-X}$, M$_X$)(Cr$_{50-X}$, M$_X$), and were produced in arc melting furnace. The as-cast alloys were cold rolled by the height reduction of 50 % and equilibrated at 973 K and 1073 K for up to 1000 h to obtain σ single phase structure, with and without prior homogenization treatment at from 1273 K to 1523 K. Phase compositions analysis and identifications in annealed alloys were conducted by EPMA and powder XRD technique respectively. Obtained XRD profiles were further analyzed by means of Rietveld method. During the analysis, crystallographic parameters of lattice constants and site occupancies in non-equivalent five sub-lattice sites (M1, M2, M3, M4 and M5) were refined. It was found that lattice expansion and shrinkage of σ phase with changing composition were reasonably explained only by considering relative size difference between constituting and solute elements. i.e. larger elements like Mo expand lattice uniformly and smaller elements like Co or Ni do in opposite manner. On the other hand, when the specific type of the elements such as Fe or Si coming into the σ phase, lattice parameter ration c/a shows increase with increasing c axis and decreasing a axis. The nonuniformity cannot be explained only by consideration of atomic size, and other factors such as magnetic or interatomic interaction could be involved. Combined with X-ray profile analysis, it was implied that the origin of crystallographic anisotropy is a characteristic site occupation behavior of the specific elements. The relations between preferential site occupation and its crystallographic features will be discussed in detail.

PM06.05.17

Refinement of Crystal Structure of Highly Ordered η–derivative Phase <u>Ryutaro Sakai</u>[1], Masaya Higashi[1], Kodai Niitsu[1,2] and Haruyuki Inui[1,2]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

Hot dip aluminized steels are practically used as automotive exhaust system parts because of their good heat resistance, corrosion resistance and designability. The coating layers have been believed to mainly consist of a thick η-Fe_2Al_5 phase and a thin θ-Fe_4Al_{13} phase. The orthorhombic η-Fe_2Al_5 (space group *Cmcm*) comprises chains of atoms with partial occupancies along the *c*-axis. Recent studies report that these sites are ordered with different manner in relation to compositions, and that there are variations of ordered phases such as the η' and η'' phases, which possess the framework structure of the η phase. Furthermore, another derivative of the η phase (the η''' phase) is suggested to exist by means of powder X-ray diffraction (XRD) analysis. However, the reported structure does not seem to be consistent in terms of the hierarchical ordering of the η phase. In this study, crystal structure of the η''' phase is assessed by means of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and XRD analysis. Ingot with Al-rich composition Fe-73.7 at.%Al was prepared by arc-melting method. After solution treatment at 1073 K for 8 hours, the ingot was encapsulated in vacuum-sealed quartz ampoules and heat-treated at 523 K for 60 days followed by water quenching. Thin foils for TEM and STEM observations were prepared by electro-polishing.
In the selected-area electron diffraction (SAED) patterns obtained from various incidence azimuth, there are superlattice diffraction spots in addition to fundamental ones of the η structure. For example, the superlattice diffraction spots are located at the positions that divide the distance between the 000 and 1-11 or 3-11 fundamental spots by two. From STEM observations, it is clarified that the η''' phase accompanies orderings of the atom sites with partial occupancies as those of the η' and η'' phases. Furthermore, the η''' phase contains periodic anti-phase boundaries (APBs) normal to the *c* axis. According to the analysis of XRD pattern, APBs are presumably introduced to compensate for the *c*-axis lattice incompatibility among adjacent η, η' and/or η'' phases.

PM06.05.18

Plastic Deformation Behavior of Single-Crystalline Micropillars of the Fe-Cr Sigma Phase <u>Masaomi Okutani</u>[1], Nobuyuki Kadota[1], Kyosuke Kishida[1,2] and Haruyuki Inui[1,2]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan.

The so-called sigma phase has long been considered to cause detrimental influences on the mechanical properties of stainless and heat-resistant steels mainly because of its high hardness and brittleness at room temperature that stem from its complex crystal structure ($D8_b$ structure, *tP*30, space group: $P4_2/mnm$, c/a ~0.52). Recently, it has been reported that the creep strength, ductility, yield strength and tensile strength of stainless steels can be improved if the distribution and morphology of the sigma phase are properly controlled. These results have caused a growing demand for fundamental understanding of plastic deformation behavior of the sigma phase itself. However, the deformation behavior of the sigma phase is largely unknown because of its brittleness at room temperature. Recently, micropillar compression tests of single crystals have been proved to be useful for studying fundamental deformation behavior of hard and brittle materials such as high temperature intermetallics, semiconductors and ceramics. In the present study, we have prepared single crystalline micropillars of the Fe-Cr sigma phase and compression-tested at room temperature as a function of loading axis orientation and specimen size. Plastic flow was observed at room temperature for all tested micropillars mostly exhibiting a smooth transition from elastic to plastic deformation similar to those observed for ductile materials. Four different slip systems were identified to be operative depending on the loading axis orientations. The values of critical resolved shear stress (CRSS) for the four slip systems identified are extremely high about 1.2 ~ 2.5 GPa. However, it should be noted that very good ductility more than 5 % compressive strain was achieved for most loading axis orientations tested, which clearly indicates that the Fe-Cr sigma phase is not inherently brittle at least under compressive loading.

PM06.05.19

Structural Control of Porous Nickel Aluminides Fabricated by Reactive Synthesis with Space Holder Powder <u>Asuka Suzuki</u>, Yunmao Shu, Naoki Takata and Makoto Kobashi; Nagoya University, Nagoya, Japan.

Porous metals have unique properties like ultra-low density, energy absorption, thermal insulation, sound absorption, fluid permeability, and so on. For example, the thermal conductivity of the porous metals with 80% porosity is about one tenth of the bulk metals. Transition metal aluminides like TiAl, NiAl, and Ni_3Al have high melting point, high strength, high oxidation and corrosion resistance, and low thermal conductivity. Porous transition metal aluminides, which have all of these properties, are expected as a high-strength energy absorber and a heat-resistant thermal insulator, and so on. Our group have developed a powder metallurgical process to synthesize porous titanium aluminides such as TiAl, $TiAl_3$, and Ti_3Al by combining reactive synthesis and a spacer method, and revealed the high strength of porous TiAl. In the present study, we attempted to synthesize porous nickel aluminides like NiAl and Ni_3Al through the reactive process and control their porous structure. Al powder with 2 μm in size and 99.99% in purity, Ni powder with 1 μm in size and 99% in purity, and sodium chloride (NaCl) particles with 30-50 μm in size and 99.99% in purity were used as starting powders. These powders were blended with various molar ratio of Al/Ni (3, 1, and 1/3). The volume fraction of NaCl was varied within the range of 0-80%. The blended powder was cold compacted at 25 MPa to obtain cylindrical precursors with 10 mm in diameter and height. An electric current sintering was performed under applying a pressure of 5 MPa. Temperature was raised in a rate of 0.5 K/s and held at 923 K for 10.8 ks. The sintered samples were soaked in water for 86.4 ks to leach out NaCl completely. For comparison, porous Al specimens were also fabricated by powder sintering and spacer method. X-ray diffraction measurements were performed operating at 40 kV and 20 mA with a Cu-Kα radiation in order to confirm the constituent phase. The porous structures of fabricated samples were observed with a scanning electron microscopy. Synthesized porous nickel aluminides had bi-modal pore size distribution. Large pore replicated the shape of NaCl particles. Small pore (0.5~4.0 μm in diameter) derived from reactive synthesis are formed where Al particles existed before the reaction. As the size of Al particles was larger, the size of small pores increased. Porosity of small pores increased with increasing the Al/Ni molar ratio. The porous structure can be controlled by the size and the composition of the starting powders.

PM06.05.20

Micropillar Compression Deformation of Single-Crystals of Cementite Fe_3C <u>Nobuyuki Kadota</u>[1], Kyosuke Kishida[1,2], Haruyuki Inui[1,2] and Wei Chen[2,3]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan; [3]School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, China.

Pearlitic steels with a lamellar structure composed of alternating ferrite and cementite (Fe_3C) layers are widely used as high-strength steel wires and rails because of their high strength. The strength of pearlitic steel wires has been known to be improved further by drawing, which makes their lamellar structure much finer. These attractive mechanical properties related to their microstructure evolution during drawing have been considered to be strongly influenced by the mechanical properties of cementite. Cementite has the orthorhombic $D0_{11}$ structure (o*P*16, space group: *Pnma*, a = 5.08, b = 6.73, c = 4.52Å), which is composed of corner- and edge-sharing carbon-centered trigonal prisms. Cementite has been considered to be brittle mainly because of its complex crystal structure with low symmetry. However, inherent deformation mechanisms of cementite Fe_3C are still largely unknown, except for some implications of

plastic deformation observed as slip band propagation across very thin Fe_3C lamella in pearlite grains and the thickness reduction of Fe_3C lamella during the drawing process of pearlitic steel wires. This is mostly because of the lack of systematical studies using single crystals. Recently, micropillar compression tests have been proved to be useful in studying deformation behavior of various crystalline materials including those with serious difficulty in preparing bulk single crystals. In this study, single crystalline micropillars of cementite were fabricated by focused ion beam technique, and tested in compression at room temperature as a function of loading axis orientation and specimen size. Plastic deformation was observed at room temperature for all tested specimens. Five different slip systems were identified experimentally for the first time. The values of critical resolved shear stress for the five slip systems were confirmed to be very high about $1.0 - 2.0$ GPa. Characteristics of identified slip systems such as actual glide plane and dislocation dissociation scheme were investigated by both experimentally through TEM analysis and theoretically by first-principles DFT calculations of generalized stacking fault energy.

PM06.05.21
Intermetallic Formation at Deeply Supercooled Ni/Al Multilayer Interfaces—A Molecular Dynamics Study Peng Yi, Michael L. Falk and Timothy P. Weihs; Johns Hopkins University, Baltimore, Maryland, United States.

Reactions at interfaces between different solid phases are critical processing steps for a variety of applications including microelectronics, superconducting magnet wires, coatings on turbine blades, and reactive materials. Due to the highly non-equilibrium nature of interfaces between metastable solid phases, phase formation at these interfaces is complicated and difficult to predict. It is well established experimentally that the first phase to form through an interfacial reaction need not be the most stable phase predicted by the phase diagram. As an example, DSC and TEM experiments in the Ni/Al multilayer system have suggested that the formation of intermetallic phases can be suppressed by a high heating rate, or by reducing the interspacing between the layers.[1, 2] Two possible mechanisms were proposed to explain phase selection for interfacial reactions: a growth-controlled mechanism[3], and a nucleation-controlled mechanism.[4]

Here we use molecular dynamics simulations to study the formation of the non-stoichiometric intermetallic compound, NiAl (B2), in the Ni/Al multilayer system, focusing on how composition gradients at the Ni/Al interfaces impact intermetallic formation.[5] Simulations were designed to study intermetallic formation under isothermal conditions within a constant composition gradient (10^8-10^9 m^{-1}) that mimics those found in nature when Al and Ni layers inter-diffuse. Simulation temperatures of 800K and 650K were chosen so as to be above and below the compositionally-dependent melting point of Al-Ni solid solution. We observed melting or amorphization at the interface region due to intermixing at 800K or 650K, respectively. The intermetallic phase then forms at the interface from the melted or amorphous region through heterogeneous nucleation, followed by growth in both lateral and normal directions. Kinetics of the transformation follows the Johnson-Mehl-Avrami model and an Avrami exponent of 0.5 was extracted from the data obtained at 800K, and 0.1 for 650K. The NiAl formation is growth-controlled and the growth rate is found to increase with decreasing composition gradient. Our finding supports a growth-competition mechanism of phase selection for interfacial reactions, which might be favored at deep undercooling.

1. Blobaum, K.J., et al., Acta Materialia, 2003. **51**(13): p. 3871-3884.
2. Grapes, M.D., et al., Thermochimica Acta, 2017. **658**: p. 72-83.
3. Thompson, C.V., Journal of Materials Research, 1992. **7**(02): p. 367-373.
4. Desré, P.J. and A.R. Yavari, Physical Review Letters, 1990. **64**(13): p. 1533-1536.
5. Yi, P., M.L. Falk, and T.P. Weihs, to be submitted.

PM06.05.22
Atomistic Kinetic Monte Carlo Modeling of the Formation of G.P. Zone in Al-Cu Alloy Hiroshi Miyoshi[1], Akio Ishii[3], Hajime Kimizuka[3] and Shigenobu Ogata[3, 2]; [1]Graduate School of Engineering Science, Osaka University, Osaka, Japan; [2]Kyoto University, Kyoto, Japan; [3]Osaka University, Osaka, Japan.

Al alloys are widely used as key structural materials especially in aerospace and automobile industries owing to their light weight, high strength, and good workability. In Al alloys, nanosized clusters of solute atoms called Guinier-Preston (G.P.) zones play a significant role in the precipitation hardening effect, in which the Cu nanoclusters impede the movement of dislocations in the Al matrix while maintaining balanced strength and ductility. Thus, it is important to control the size, orientation, and shape of the nanoclusters for the adequate design of Al alloys. The observations with high-resolution transmission electron microscopy revealed that the structures of G.P. zones consist of disk-shaped, monoatomic layered precipitates of Cu atoms along the {100} planes. However, the detailed mechanism of the formation of the zones has not been clarified yet. Understanding of the atomistic mechanism may serve as relevant information for the design and exploitation of advanced Al alloys with excellent mechanical performance.
In this study, in order to elucidate the atomistic behavior of solute atoms and vacancies in the process of the formation of G.P. zones, a framework of atomistic kinetic Monte Carlo modeling for Al-Cu alloys was developed based on density functional theory (DFT). An on-lattice potential model for a dilute Al-Cu-vacancy system was constructed using the DFT-calculated binding energies for the pairs and triplets of Cu atoms and a vacancy in the Al matrix, and then applied to atomistic kinetic Monte Carlo calculations. The DFT results revealed that the Cu-Cu pairs in the first-nearest neighbor (1NN) position and the Cu triplets with a 1NN bond angle of approximately 90 degree exhibit significant attractive interactions whereas a vacancy does not prefer to occupy sites neighboring to these Cu pairs and triplets. This suggested that a vacancy can diffuse rather randomly without strong bindings to Cu atoms and that Cu atoms gradually form clusters via a vacancy-assisted diffusion mechanism with a lowering of the energy of the system. Indeed, the results of atomistic kinetic Monte Carlo calculations supported this view and reproduced the planar segregation of Cu atoms along the {100} planes in a manner consistent with experimental measurements. Also, the effects of temperature and vacancy concentration on the formation of G.P. zone were investigated. The nucleation behavior of G.P. zone obtained from the kinetic Monte Carlo analysis was compared with the counterpart based on classical nucleation theory. The critical nucleus size for the formation of G.P. zone was estimated from the formation free energy of Cu clusters with considering a competition between the enthalpic and entropic contributions to the free energy at finite temperatures.

PM06.05.23
Micromechanical Characterization of Long-Period Stacking Ordered Phase-Based Mg Alloy Single Crystals Kosuke Takagi, Tsuyoshi Mayama, Yoji Mine and Kazuki Takashima; Department of Materials Science and Engineering, Kumamoto University, Kumamoto, Japan.

Long-period stacking ordered (LPSO) phase is an intermetallic compound in high-strength Mg alloys such as $Mg_{97}Zn_1Y_2$. Basal slip acts as the primary deformation mode in the LPSO phase because of its lower critical resolved shear stress than the others, leading to the formation of slip and kink bands, which are macroscopically parallel and perpendicular to the basal plane, respectively. Although the formation of these deformation bands may be triggered by the activation of basal slip, they have still not been understood. We performed a micro-tensile test combined with crystal plasticity finite element method (CPFEM) of the single-crystalline 18R-type LPSO phase with several loading axes to clarify the differences between the slip band and kink band formations.
The material used in this study was a directionally solidified $Mg_{85}Zn_6Y_9$ (at.%) alloy, composed of nearly single-phase LPSO microstructure. The crystal orientation of the alloy was determined by electron backscatter diffraction (EBSD) analysis. Micrometer-sized tensile specimens with gauge section

dimensions of $20 \times 20 \times 50$ μm^3 were fabricated using focused ion beam. Some specimens were prepared such that their loading axes were inclined at 14° – 60° to [0001] direction. Micro-tensile tests were performed at a displacement rate of 0.1 $\mu m/s$ at room temperature in atmospheric air. CPFEM analysis models of the tensile specimens were uniformly divided into 6400 elements, and Euler angles obtained from EBSD analysis were allocated to each element.

For the 45° and 60° specimens, the basal slip was localized at the onset of yielding, followed by strain softening. Transmission electron microscopy observation revealed the formation of basal dislocation network within the slip band, suggesting that basal slips with different <11-20> Burgers vectors were activated in spite of single basal slip conditions. Considering the strain softening, CPFEM analysis demonstrated the slip localization attributed to simultaneous occurrence of basal slips containing three <11-20> Burgers vectors. Since the chemical modulation of Zn and Y atoms are periodically developed on the (0001) plane of LPSO structure, cross slipping of basal dislocation onto prismatic plane hardly occurs, which promotes the coplanar basal slip gliding. In contrast, the 14° specimen exhibited kink band formation coincident with the stress drop, which resulted in a sudden crystal rotation. CPFEM analysis was well consistent with the experimental deformation behavior, and revealed that stress concentration perpendicular to the basal plane was generated prior to the stress drop. These findings suggest that basal dislocations were locally activated along the region where the stress highly concentrated, and subsequently accumulated at the boundary between concentrated and unconcentrated regions, which resulted in the kink boundary.

PM06.05.24

Microstructures and Their Thermal Stability of Al-Based Eutectic Alloys Strengthened by Intermetallic Phases in Al-Zn-Mg Ternary System <u>Taiki Okano</u>, Naoki Takata, Asuka Suzuki and Makoto Kobashi; Department of Materials Process Engineering, Nagoya University, Nagoya-shi, Japan.

Since aluminum (Al) alloys have high specific strength, it is used in the compressor wheel of vehicle turbochargers which is required to be lightweight. This part is exposed to high temperature with the compression of air, and it reaches up to about 200 °C. However, when Al alloys which are strengthened by fine metastable precipitates are kept at elevated temperatures, the metastable phases transform into coarse stable phases after long-term exposure. Thus, low microstructural stability of the Al alloys significantly reduces their strength at elevated temperatures. On the other hand, the commercial refractory metals and alloys (e.g. Ni-based superalloys) contains stable intermetallic phases with a high volume ratio of 50% or more as a strengthening phase, resulting in maintaining high strength even at high temperature. In this study, we designed two Al-based cast alloys strengthened by thermodynamically stable intermetallic phases with a high volume fraction.

We focused on eutectic reactions in order to have high volume fractions of intermetallic phases. We selected two commonly used metals, Zn and Mg, as alloying elements, and attempted to fabricate two types of α-Al (fcc) matrix reinforced by η-Zn_2Mg (hexagonal) and T-$Al_6Mg_{11}Zn_{11}$ (cubic) intermetallic phases. Thermodynamic assessments revealed two alloy compositions of Al-36Zn-18Mg and Al-23.5Zn-22.5Mg (at%) with the α-Al (fcc) phase reinforced with high fractions (>50%) of the η and T phases. The morphology of the α-Al phase in the eutectic colonies varied upon changing the neighboring intermetallic phase. The lamellar structure consisting of α-Al and η phases appeared in a large part of the cast Al-36Zn-18Mg alloy. In the cast Al-23.5Zn-22.5Mg (at%) alloy, rod-shaped α-Al phase was observed within T-phase matrix in the eutectic microstructure. These eutectic microstructures exhibit high stability at an elevated temperature of 300 °C. It was found that the solidification segregation of Zn component was observed around the eutectic cell boundaries in the Al-36Zn-18Mg alloy. The microstructural observation of the alloy exposed at 300 °C confirmed that the Zn-enriched regions would enhance the local microstructural change at elevated temperatures. This result demonstrates that the Al-23.5Zn-22.5Mg (at%) alloy is superior to the Al-36Zn-18Mg (at%) alloy in terms of microstructural stability at elevated temperatures. The fabricated alloys exhibited high hardness values exceeding 220 HV, which were much superior to those of conventional Al alloys. These alloys exhibited high hardness values exceeding 200 HV even after the exposure at 300 °C for 1000 h. In this presentation, crystallographic features of these eutectic microstructures will be presented in conjunction with transmission electron microscopy.

PM06.05.25

Effect of Intermetallic Compound YAl_2 Particles on the Corrosion Behavior of Mg-Li Matrix Composite <u>Zihan Chen</u> and Chonggao Bao; Xi'an Jiaotong University, Xi'an, China.

Mg-Li based alloys are currently the lightest among the metallic structural materials, and they have many excellent properties such as high values specific strength, mechanical casting properties, good damping capacity, good thermal conductivity and electromagnetic shielding performance. The strength of Mg-Li alloy is greatly improved by the composite strengthening of intermetallic compound YAl_2 particles, but the low corrosion resistance of Mg-Li alloy is still the main factor that restricts the application of the alloy and its composites. The effect of intermetallic compounds YAl_2 particles on corrosion behavior of Mg-Li matrix composite (YAl_{2p}/LA143) in 3.5wt.% NaCl solution was systematically investigated. Microstructure was examined by Electron microscope, X-ray diffraction, and 3D laser scanning microscope. Corrosion performance was evaluated by immersion tests, electrochemical measurements , and direct visual observation. The results showed that the corrosion resistance of YAl_{2p}/LA143 composite improved significantly as the formation of a transitional interface layer by adding YAl_2 particles. The diffusion of yttrium and aluminum atoms from YAl_2 particulates improved the stability of the surface film and enhanced the adhesion between the corrosion products and the substrate, which hindered the further expansion of pitting.

PM06.05.26

Thermodynamics and Kinetics of Bimetallic Nanoparticles from First Principles Calculations <u>Shubham Pandey</u>[1], Robert Koch[2], Guangfang Li[3], Hui Wang[3], Scott Misture[2] and Simon R. Phillpot[1]; [1]Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States; [2]Inamori School of Engineering, Alfred University, Alfred, New York, United States; [3]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, United States, Columbia, South Carolina, United States.

We use Density Functional Theory (DFT) to characterize the energetics of Cu-Au and Ni-Au ordered alloys and the effects of epitaxial strain on their relative stabilities. We find that epitaxy on a Au substrate tends to destabilize Cu-rich alloy structures, while having little effect on Au-rich alloys. Work of adhesion is used to characterize the interfacial stability and we find higher works of adhesion for alloys grown expitaixally on Au, than on Cu or Ni. Diffusion in bulk intermetallics, random alloys and at epitaxial interfaces is analysed. Diffusion across the Cu-Au [111] interface is modeled for Au substrate where we find that, there is a barrier for Cu diffusion while Au diffusion is barrierless. Random alloys give identical migration barriers for both Cu and Au, and follow a Gaussian distribution. The computational results are correlated with experimental analysis of phase stability and kinetics in the corresponding nanoparticles.

PM06.05.27

Phase-Field Modeling of Evolution of Compact Ordered Precipitates in Ternary Alloy Systems <u>Sandeep Sugathan</u> and Saswata Bhattacharya; Department of Materials Science and Metallurgical Engineering, Indian Institute of Technology, Hyderabad, Hyderabad, India.

Several technologically important alloys exhibit compact precipitates in their microstructure. For example, ternary Al-Sc-Li alloys form coherent $L1_2$ precipitates of Al_3Li and $Al_3(Sc,Li)$ during a two-step ageing process [Radmilovic et al., Nature Materials **10**, 710 (2011)]. Al_3Li phase envelops the $Al_3(Sc,Li)$ phase giving rise to a compact core-shell morphology with strong monodispersity. Modified Inconel 718 also exhibits a compact morphology where three orientational variants of γ'' envelop cuboidal γ' precipitates [Cozar, R. and Pineau, A., Metall. Trans. **4**, 47 (1973)] . Factors affecting the formation of such precipitates include alloy chemistry, relative interfacial energies between the coexisting phases, elastic misfit and solute diffusivities. We present a phase-field model in two dimensions to study the effects of alloy chemistry, interfacial energy and elastic stress (arising due to coherency) on the morphological evolution of compact precipitates. The model employs a modified regular solution description of the bulk free energy of the disordered matrix phase and ordered precipitates with coefficients obtained from the thermodynamic data for the relevant systems. Elastic strain energy of the three-phase system is described using Khachaturyan's microelasticity theory. The temporal evolution of the spatially dependent field variables is determined by numerically solving coupled Cahn-Hilliard and Allen-Cahn equations for composition and order parameter fields, respectively. We use a semi-implicit Fourier spectral scheme to integrate the governing equations. We systematically vary the gradient energy coefficients and misfit strains to study their effect on the development of compact precipitates. Further, we vary the mobilities of diffusing species in order to understand their effect on the stability of compact morphology. The sign and degree of misfit as well as the relative interfacial energies between the phases affect solute partitioning, thereby influencing the formation of compact morphology. Our simulations show the development of stable core-shell morphology when the misfit between the ordered precipitate phases is lower than those with the matrix phase although the interfacial energies between the coexisting phases do not satisfy the wetting condition proposed by Cahn [J.W. Cahn, J. Chem. Phys. **66**, 3667 (1977)]. Thus, the elastic interactions between the phases is a crucial factor affecting the stability of "monodisperse" core-shell microstructures. We further conclude from our simulations that low mobility of solute atoms forming the core lead to sluggish coarsening of compact core-shell structures.

PM06.05.28

Superelasticity in Micro/Nano Pillars of Cu-Al-Be Shape Memory Alloys Valeria Fuster[3, 1], Jose F. Gómez-Cortés[1], Maria L. No[2] and Jose San Juan[1]; [1]Fisica Materia Condensada, Universidad del Pais Vasco, Bilbao, Spain; [2]Fisica Aplicada II, Universidad del Pais Vasco, Bilbao, Spain; [3]Instituto de Fisica Rosario, Universidad Nacional de Rosario, Rosario, Argentina.

Shape memory alloys are functional intermetallics which undergo a reversible martensitic transformation responsible for the shape memory and superelastic effects. In addition, shape memory alloys offer the highest workoutput density, in comparison with other smart materials, and consequently are firm candidates to be incorporated as sensors and actuators into MEMS and NEMS because of their ability to undergo the thermal or stress-induced martensitic transformation (superelastic) with a high-displacement actuation. A good shape memory behaviour and superelasticity were recently reported in Cu-Al-Ni SMA [1, 2, 3]. However, among the different explored alloy families, up to now Cu-Al-Ni is the only SMA system exhibiting good properties at nano-scale.
The aim of the present work is to explore a new SMA system, and to this purpose [001] oriented D03 single-crystals grown from a Cu-12.0Al-0.47Be (wt.%) shape memory alloy were synthesized in our laboratory. This alloy has the martensitic transformation temperatures below room temperature, showing excellent superelastic properties at macroscopic scale. Then, in the present study we carried out a quantitative characterization and analysis of the superelastic behaviour at the micro and nano scale. A series of pillars covering a broad-range of size diameters, between 265 nm and 1.800 μm, were milled by Focused Ion Beam (FIB) from single crystal slides. These pillars were studied by hundreds of nano-compression cycles at room temperature using instrumented nanoindentation. Our results show that this alloy also exhibits an excellent superelastic behaviour at small scale, as well as a size effect on the critical stress to induce the transformation. In addition, the analysis of such size effect shows that the critical stress follows a power-law type as a function of the pillar diameter, in agreement with recent reports in the Cu-Al-Ni system [3]. These results seems to confirm the universality of the power law found in Cu-based SMA, and open the door for future small-scale applications.

[1] J. San Juan, M.L. Nó, C.A. Schuh, Nature Nanotechnology 4, 415 (2009).
[2] J. San Juan et al., Applied Physics Letters 104, 011901 (2014).
[3] J. Gómez-Cortés et al., Nature Nanotechnology 12, 790 (2017).

PM06.05.29

Isothermal Martensitic Transformation Behavior of NiCoMnIn Metamagnetic Shape Memory Alloy Yoshiki Yano[1], Kodai Niitsu[1], Ryosuke Kainuma[3] and Haruyuki Inui[1, 2]; [1]Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; [2]Center for Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto, Japan; [3]Department of Metallurgy, Materials Science and Materials Processing, Tohoku University, Sendai, Japan.

Dynamics of thermo-elastic martensitic transformations (MTs) is described by the nucleation and growth processes, and in particular the former is associated with only the forward transformation. In relation to this, isothermal forward MT behavior with a C-shaped curve in TTT (Time-Temperature transformation) diagram has been discussed in terms of the thermal activation process of nucleation, but not studied for the reverse MT. Considering the dominance of nucleation process is different with respect to the direction of MTs, isothermal dynamics of the reverse MT is expected not to be the same as that of the forward one.
In the present study, we investigated the isothermal and non-isothermal behaviors of magnetic-field-induced martensitic transformation in $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ metamagnetic shape memory alloy. Non-isothermal MT was performed for various scanning routes of temperature and magnetic field to figure the phase diagram. Isothermal MT was examined by settling magnetic field and temperature at various stages of forwarding/reversing MTs. Isothermal holdings showed logarithmic evolutions of transforming fraction both in the forward/reverse MTs. However, its temperature and time dependences were in contrast with respect to transforming directions; while isothermal forward MT showed iso-fraction C-shaped curves in the TTT diagram as reported elsewhere, isothermal reverse MT showed only lower half of C-shaped curve that terminates at the reverse MT finishing temperature. This alloy is known to show an increasing MT hysteresis upon cooling due to the development of thermal activation nature of MT. By decomposing the hysteresis into thermal activation and non-thermal activation components, the origin of different isothermal MT behaviors between forward/reverse MTs was discussed. We propose a new formula that can describe the dynamics of forward/reverse isothermal MTs simultaneously by taking into account the thermal and non-thermal activation processes of nucleation and growth.

PM06.05.30

Influence of NiAl Precipitation on the Martensitic Transformation of Cu-Al-Ni Shape Memory Alloys Nora Egido[1], Jose San Juan[2], Isabel Ruiz-Larrea[1], Mariano Barrado[3], Tomasz Breczewski[1] and Maria L. No[1]; [1]Física Aplicada II, Universidad del Pais Vasco (UPV/EHU), Bilbao, Spain; [2]Física de la Materia Condensada, Universidad del Pais Vasco (UPV/EHU), Bilbao, Spain; [3]SGIKER Microscopia Electrónica y Microanálisis de Materiales, Universidad del Pais Vasco (UPV/EHU), Bilbao, Spain.

Shape memory alloys (SMAs) exhibit a diffusionless martensitic transformation (MT) between the high-temperature phase (austenite) and the low temperature phase (martensite). SMAs have recently attracted renewed interest from the scientific community as a result of their behavior and properties at micro and nano scales [1,2]. At present the technological applications of SMA are based on superelastic, pseudoelastic and shape memory

thermomechanical properties and in particular the CuAlNi SMAs with small amounts of Ni show their best properties as single crystals without α and γ$_1$ precipitates. The CuAlNi is an dordered L2$_1$ phase that transform during cooling to an ordered β'$_3$ monoclinic martensite or to an ordered γ'$_3$orthorhombic martensite or to both of them.

With the idea that NiAl B2 precipitates could improve the mechanical properties of the CuAlNi SMAs, by hardening the austenite phase, in the present research work the influence on the thermal martensitic transformation of larger amounts of Ni and their precipitation as NiAl, has been studied. The best temperature, thermal treatment and quenching process has been determined in order to avoid the precipitation of the other non desirable stable phases γ$_1$ and α.

Oriented [001]$_{L21}$ single crystals with 26,26Al-5,05Ni-68,69Cu (At.%) were used in the present work. Internal friction (IF) experiments were employed to optimize the thermal treatments and temperatures in order to obtain and control the NiAl precipitation. The microstructure of the as-quenched samples from 1173K, without precipitates, and the thermally treated samples, with precipitates, were determined by different techniques of scanning electron microscopy (SE, BSE, EBSD) focus ion beam (slice mode) and transmission electron microscopy (BF,DF, STEM-HAADF, EDX) with a philips CM-200 and a TitanCubed 80-300KV with the super-X detector ChemiSTEM. The results show us that it is possible to control the density and the size of NiAl precipitates avoiding the α and γ$_1$ stable phases and preserving the martensitic transformation.

[1] J. San Juan, M. L. Nó, C. A. Schuh, Advanced Materials 20 (2008) 272
[2] J. Gómez-Cortés, M.L. Nó, I. López-Ferreño, J. Hernández-Saz, S.I. Molina, A. Chuvilin, J. San Juan. Nature Nanotechnology 12 (2017) 790-796

PM06.05.31

Mechanical Properties of Au–Cu–Al Biomedical Shape Memory Alloys Containing Ag Ayano Toriyabe[1], Kenji Goto[1, 2], Akira Umise[1, 3], Hiroyasu Kanetaka[4] and Hideki Hosoda[1]; [1]Institute of Innovate Research (IIR), Tokyo Institute of Technology, Yokohama, Japan; [2]Tanaka Kikinzoku Kogyo K.K., Isehara, Japan; [3]Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Chiyoda, Japan; [4]Graduate School of Dentistry, Tohoku University, Sendai, Japan.

AuCuAl alloy is a promising shape memory alloy which is suitable to X-ray radiography and magnetic resonance imaging. In order to enhance biocompatibility and antibacterial activity of AuCuAl alloy, Ag addition to AuCuAl alloy was focused in this study. Because Ag ions released from material bring strong antibacterial effect in human body. However, the effect of Ag addition to AuCuAl of phase constitution, transformation behavior and mechanical properties has not been reported in the literature. Then, mechanical properties of AuCuAl containing Ag were investigated in this study. Several AuCuAl alloys containing Ag in which Ag is expected to substitute for the Au sites and Cu sites were fabricated by Ar arc-melting method. They were hot-forged at 873K and solution-treated at 773K for 3.6ks followed by iced water quenching. Phase constitution, transformation temperatures, microstructure and chemical compositions were evaluated by θ-2θ X-ray diffractometry (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy, respectively. Mechanical properties were evaluated by micro Vickers hardness tests and tensile tests, compression tests at room temperature.

The phase constitution of 45Au–20Cu–25Al–5Ag and 50Au–25Cu–25Al–5Ag alloys was L2$_1$ parent single phase at RT by XRD. However, 45Au–25Cu–25Al–5Ag alloy contained small amount of second phase by SEM. Reverse martensitic transformation finish temperature by DSC was 240K in 45Au–25Cu–25Al–5Ag and 243K in 50Au–20Cu–25Al–5Ag, which were approximately 50K lower that of the stoichiometric Au$_2$CuAl. Then, martensitic transformation temperature was decreased by Ag addition but the substitution site seems little influence. Micro Vickers hardness of 50Au–20Cu–25Al–5Ag and 45Au–25Cu–25Al–5Ag alloys was HV272 and HV236, respectively. These values were higher than HV170 of Au$_2$CuAl. By tensile tests at RT, both Ag-added alloys exhibited no plastic deformation due to the intergranular fracture, similar to the Au$_2$CuAl. The ultimate tensile strength of both alloys was 182 and 177 MPa, which was higher than that of Au$_2$CuAl. Then, Ag addition is found to enhance hardness and fracture strength of Au-Cu-Al alloys.

PM06.05.32

Ductility Enhancement of AuCuAl Biomedical Shape Memory Alloys by Introducing FCC α Phase Akira Umise[1, 2], Koki Yamaji[1], Hayato Gunji[1], Kenji Goto[1, 3], Masaki Tahara[1], Takao Hanawa[2] and Hideki Hosoda[1]; [1]Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Japan; [2]Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Chiyoda, Japan; [3]Tanaka Kikinzoku Kogyo K.K., Isehara, Japan.

Au-based shape memory alloys exhibiting good biocompatibility and excellent X-ray radiography have a large potential to exceed Ti-Ni SMAs in the field of biomedical implant devices. Especially AuCuAl alloys have attracted attention. However, based on the present available data, ternary polycrystalline AuCuAl alloys which are often brittle due to intergranular fracture. In this study we focused on introduction of second phase at grain boundaries that must enhance grain boundary cohesive strength, and mechanical properties were investigated. The second phase selected is α phase that is the fcc terminal solid solution of (Au,Cu) in the Au-Cu-Al system.

Au-33Cu-15Al (AuCuAl single phase) and Au-37Cu-15Al (AuCuAl+α two phases) alloys (hereafter, in at.%) were prepared by Ar-arc melting method using a non-consumable W electrode. Both the alloys were expected to have a similar chemical composition of AuCuAl phase. The ingots were hot-pressed at 873K for 21.6ks and solution-treated at 773K for 3.6ks followed by water quenching. Microstructural observation and chemical analysis were done by scanning electron microscopy equipped with energy dispersive X-ray spectrometry (SEM-EDX). Phase constituent and phase transformation were characterized by θ-2θ X-ray diffractometry and differential scanning calorimetry, respectively. A cyclic loading-unloading tensile test with a constant strain increment of 1% was performed at RT.

SEM and XRD analysis revealed that Au-37Cu-15Al alloy contains α phase. The chemical composition of the matrix AuCuAl and fcc a phase in Au-37Cu-15Al alloy were 48.3Au–35.3Cu-15.8Al and 45.6u-40.6Cu-13.8Al, respectively. Then, the chemical composition of matrix in Au-37Cu-15Al is close to that of Au-33Cu-15Al. Then, the difference is the presence of α phase in comparison with Au-33Cu-15Al single-phase alloy. The tensile tests revealed that the elongation of Au-37Cu-15Al alloy containing α phase was much improved: the elongation was 14% in Au-37Cu-15Al alloy and 1.8% in Au-33Cu-15Al alloy. The improvement of ductility must be achieved by the introduction of fcc a phase at the grain boundaries.

PM06.05.33

Formation of Thermally Stable Intermetallic Electrodes with Low Contact Resistance for Semiconducting Thermoelectric Mg₂Si Fuyuko Ikeda[2], Koki Kaita[1], Tomoya Kawamura[1], Daishi Shiojiri[1] and Tsutomu Iida[1]; [1]Tokyo University Of Science, Tokyo, Japan; [2]Material Science and Technology, Tokyo University Of Science, Tokyo, Japan.

Magnesium silicide (Mg$_2$Si) has some important features that make it a material that could be used for generating power from industrial waste heat by means of thermoelectric (TE) technology. First, it is a lightweight material; second, there is a worldwide abundance of its constituent elements; and third,

the production processes are non-toxic. In addition, the power generation performance in the mid-temperature (~900K) range is sufficiently good for it to be applied to waste heat recovery devices in automotive engines and industrial furnaces. We have fabricated TE devices with a highest power factor of ~4x10^{-3} W/mK^2 at ~800 K and a ZT value >1.2 at ~850 K for Mg$_2$Si co-doped Sb and Zn. To produce Mg$_2$Si TE power modules, the formation of an appropriate electrode with low contact resistance and thermal stability up to the operating temperature is needed. The method we chose for forming the electrodes, which can be adapted to large-scale production, is a metallic paste printing method. In order to realize a reproducible electrode formation process, we developed an automatic paste printing machine, with which it is possible to obtain good uniformity and to control the film thickness in a precise manner. Ni is a promising electrode metal for Mg$_2$Si, and we have used a monoblock sintering method to form electrodes during sintering of the Mg$_2$Si, and obtained electrodes with a sufficiently low contact resistivity of < 1×10^{-9} Ωm^2. However, with Ni electrodes made using the paste printing method and the subsequent calcination process we have not achieved contact resistivities < 1×10^{-9} Ωm^2 in a reproducible manner. Moreover, the formation of Ni-silicide at the Mg$_2$Si/Ni interface when the temperature reaches the operating temperature of ~900 K leads to degradation of the interface due to the formation of MgO. This is due to oxidation of the residual metallic Mg left after decomposition of the Mg$_2$Si to form Ni-silicide at the interface. Thus, combinations of Ni and some other metallic materials were examined for the electrode. In order to improve the contact resistivity and thermal stability of the electrode at elevated temperatures, Cu, Ti, Al, Au and Pd were used in the paste printing method. The powder sizes of the constituent metals in the pastes were 0.4 mm for Ni, 1.0 mm for Cu, 20 mm for Ti, 0.8 mm for Au, and 0.9 mm for Pd, and the Cu, Ti, Au and Pd contents in the pastes were varied from 0.5 to 5.0 at%. For Au, the contents were 0.5 at% and 1.0 at%, and the observed contact resistivities were 0.94×10^{-10} and 1.9×10^{-10} Ωm^2, respectively. On the other hand, with Pd included in the electrode, the contact resistivities were 0.94×10^{-10} and 0.90×10^{-9} Ωm^2, for Pd contents of 0.5 at% and 1.0 at%, respectively. In the report, we also discuss the durability when operated in air and the inter-diffusion behavior at the interface between the Mg$_2$Si and the electrode formed using the paste printing method.

PM06.05.34
Performance Improvement of Ni-Mn-Sn Magnetic Shape Memory Alloys by Co and Cu Addition Kun Zhang and Changlong Tan; Harbin University of Science and Technology, Harbin, China.

Compared to the traditional shape memory alloys (SMAs), ferromagnetic shape memory alloys (FSMAs) show a strong coupling between structure and magnetism. Except for thermal drive, FSMAs can produce force and deformations in response to a magnetic field. Recently, the applications of Ni-Mn-Sn FSMAs in actuator, sensor, and solid-state refrigerator can be expected due to their unique phase transition mechanism and rich physical properties. The low working temperature and the poor mechanical properties are the crucial problems limiting the application and development of Ni-Mn-Sn FSMAs. Moreover, to increase the working temperature, it is necessary to elevate the martensitic transformation temperature (Ms) while keeping the Curie temperature (Tc). How to solve all the problems mentioned above at the same time is the key.
In this paper, the new idea for increasing the working temperature and enhancing the mechanical properties is proposed by doping two elements simultaneously. Owing to the performance of different roles in Ni-Mn-Sn alloys, adding Co and Cu at the same time may elevate Tc while keeping the Ms high, and improve the mechanical properties of Ni-Mn-Sn alloys. The results of DSC curves show that martensitic transformation is observed in Ni$_{48-x}$Co$_x$Mn$_{37}$Sn$_9$Cu$_6$ ($x = 0$, 6, and 8 at.%) alloys. And the martensitic transformation temperatures decrease remarkably with the increase in Co content. However, the Ms of Ni$_{40}$Co$_8$Mn$_{37}$Sn$_9$Cu$_6$ alloy is still higher than 373.5 K. Furthermore, the Tc is detected by the M-T curves. It is shown that Tc increases significantly with the increase in Co content. The Curie temperature Tc increases to 391.1 K for $x = 8$, which is higher than the Ms.
In order to obtain the strength and ductility behavior of Ni$_{48-x}$Co$_x$Mn$_{37}$Sn$_9$Cu$_6$ ($x = 0$, 6, and 8 at.%) alloys, the compressive mechanical properties are tested for the alloys. The alloys were loaded at room temperature until failure in compression. The results show that the compressive stress increases from 209.7 MPa to 982.8 MPa and the compressive strain increases from 5.2% to 10.7% with increasing Co content from 0 at.% to 8 at.%. The appropriate amount of Cu and Co addition in Ni-Mn-Sn alloys enhances the compressive strength and improve the ductility.

PM06.05.35
Fabrication of Thermoelectric Power Generator Using Solely N-Type Mg₂Si for Automotive Application Tatsuya Yamashita, Kenki Tani, Daishi Shiojiri and Tsutomu Iida; Material Science of Technology, Tokyo University of Science, Tokyo, Japan.

Intermetallic silicide of magnesium silicide (Mg$_2$Si) is a promising candidate for practical thermoelectric (TE) power generation, because it has several promising features, such as the abundance of its constituent elements, its non-toxicity, and the facts that it is light weight and has the capability of generating power. For automotive applications, lighter and tougher thermoelectric power generators are advantageous; however, these applications are sometimes demanding on the devices. Mg$_2$Si has already achieved a ZT value greater than unity. In order to realize its practical use as a TE generator (TEG), both low fabrication cost and significant lifetime at an elevated operating temperature are important. We have developed an n-type Mg$_2$Si TE element as part of a feasible TE device. There are economic advantages to using Mg$_2$Si in thermoelectric devices. Basically, the p-type conductivity of Mg$_2$Si is possible but the thermoelectric properties of p-type material are not equivalent to that those of n-type Mg$_2$Si one. Therefore, a so-called "unileg" device structure, incorporating only an n-type Mg$_2$Si TE leg, is one possible solution to realizing practical Mg$_2$Si TEGs. Compared with the conventional p-structure TE module, which comprises both p- and n-type TE elements, the uni-leg structure alleviates the problems associated with the difference in thermal expansion between p- and n-type TE elements at high temperature. To reduce the electrical and thermal contact resistance of the module, each part of the module was joined using new soldering intermetallic alloys. We are currently tuning the TE chip power generation ability by modifying the type of dopant and the contents of the matrix and the TE chip dimensions. The elemental n-type Mg$_2$Si TE chip, which is doped by donor impurities with dimension of 5x5x5 mm^3, exhibits power generation density of 4.1 W/cm^2 over a temperature difference at between 873 K and 373 K (DT= 500 K). Using this TE chip, a prospective unileg structure TE module consisting of the arrangement of 6 TE chips in a line as a basic TEG structure. The thermal distribution and power generation characteristics for the fabricated unileg TEG was analyzed using finite element modeling using the ANSYS code, and heat transfer analysis to understand the thermal impedance characteristics using the Flow Designer code. A making a consistency between the calculation parameters of the ANSYS and the Flow Designer and the fabricated TEG, precise measurements of the temperature, heat flow, and power generation at various probe points on the module were made. Fabricated TE module were examined for vibration test corresponding to automotive test procedures. Moreover, results obtained from automotive engine simulation using GT-POWER will be also discussed in terms of power generation ability and adaptability for attaching to automotive exhaust line.

PM06.05.36
Synthesis of N-Type Mg₂Si Using Conventional Vertical Bridgman Method for Thermoelectric Power Generation Application Hiroto Hamba, Takuya Kodama, Daishi Shiojiri and Tsutomu Iida; Material Science and Technology, Tokyo University of Science, Tokyo, Japan.

Magnesium silicide (Mg$_2$Si) has been identified as a promising advanced thermoelectric (TE) material and it has some important attributes in that it is lightweight, there is a worldwide abundance of its constituent elements, and it is non-toxic. Moreover, since it has good power generation performance in the mid-temperature (~900K) range, it is expected that it can be applied in the automotive industry or in industrial furnaces. The current status for Mg$_2$Si is aimed toward TE module fabrication and appropriate system integration techniques for electric vehicle (EV) range-extender waste- heat recovery applications. For the industrialization, thermal stability under the practical operation temperatures is needed to ensure the power generation durability. Mg$_2$Si is its capability for being doped in order to modify its electrical conductivity, thermal conductivity and durability at elevated operating temperatures.

Typically, impurity elements were introduced into a congruent melt of Mg_2Si using the "All Molten Synthesis" method. Then, the resultant polycrystalline Mg_2Si was pulverized and then sintered using a "Plasma Activated Sintering" (PAS) technique to form a TE power generation chip. However, we have been trying to establish a TE chip fabrication directly from melt synthesis Mg_2Si, so polycrystalline Mg_2Si by all-molten synthesis using Bridgman method is performed. For the industrialization of Mg_2Si TE chip for generator, thermal stability at the practical operation temperatures is predominant requirement, thus a synthesis possessing with a thermodynamically stable grain boundary were made with less process contaminant. Because the instrument of oxidation of residual Mg during synthesis process is seen to be closely associated with an onset of degradation. Typically, degradation of the Mg_2Si TE chip begins from MgO located at grain boundaries and proliferate to the periphery, when the TE chip is elevated up to mid-operation temperature. Thus, we are interested in an elimination of residual metallic Mg or MgO at grain boundary, namely, an obtaining thermally stable grain boundary of polycrystalline Mg_2Si by all-molten growth method. The examined Mg_2Si grown specimens were heavily doped with donor impurities of Sb and isoelectric impurity of Zn to enhance their power generation characteristics. In this report, we discuss about crystalline quality, doping behavior and corresponding TE properties (Seebeck coefficient, electrical conductivity, thermal conductivity, power factor and figure-of-merit), thermal durability of all-molten synthesized polycrystalline Mg_2Si.

PM06.05.37
Nanocrystallization and Recoilless Fraction Determination of Fe68.5Co5Nb3Cu1Si15.5B7 Ferromagnetic Alloy <u>Monica Sorescu</u>[1] and Kevin Byerly[2]; [1]Duquesne University, Pittsburgh, Pennsylvania, United States; [2]NETL, Pittsburgh, Pennsylvania, United States.

Amorphous alloy Fe68.5Co5Nb3Cu1Si15.5B7 was obtained by melt spinning. Samples cut from the foil were annealed at 450, 550, 650 and 750 C in a vacuum furnace. 57Fe Mossbauer spectroscopy was used to identify the crystalline phases formed and the orientation of the magnetic moments based on the refined values of the hyperfine parameters. The as-quenched sample was analyzed with a hyperfine magnetic field distribution and corresponded to an in-plane orientation of the magnetic moment directions. Similar field distribution and moment orientation were obtained for the specimen annealed at 450 C, while for the Fe56Co24Nb4B13Si2Cu1 system analyzed previously we obtained the onset of nanocrystallization at this annealing temperature. The sample annealed at 550 C exhibited the nanocrystalline state formation due to the obervation of the DO3 structure of the Fe-Si alloy with small amounts of Co replacing Fe in the composition. Five distinct sextets in the Mossbauer spectra could be assigned to D+A8+A7, A6, A5, A4 and a metalloid enriched amorphous grain boundary phase. The relative line intensities showed that the magnetic moments were distributed at random. The spectra of the samples annealed at 650 and 750 C were also indicative of nanocrystallization, with the magnetic moments reoriented out-of-plane for the last sample. This behaviour is in contradistinction with that of the Co-rich system, which was totally crystallized at these annealing temperatures. Our results show that small Co additions can lead to the formation of nanostructures over a whole range of annealing temperatures.
A new series of Mossbauer spectra was obtained by recording simultaneously the intensity transmitted by a superposition of the sample with the stainless steel etalon, based on the dual absorber method recently introduced by us. The values of the recoilless fraction could be derived from the relative spectral areas. The f factor maintained values close to 0.7 for all samples measured, but dropped to 0.37 for the sample annealed at 750 C. This behavior could be related to the presence of elastic stresses in the system, which caused the out-of-plane reorientation of the magnetic moment directions.

PM06.05.38
Fabrication and Mechanical Thermoelectric Properties of Mg_2Si Reinforced with Intragranular SiC Nano Particles <u>Junki Nakano</u>, Ryo Inoue, Tsutomu Iida and Yasuo Kogo; Tokyo University of Science, Tokyo, Japan.

Thermoelectric (TE) materials could play an important role in a global sustainable energy solution. Magnesium silicide (Mg_2Si) is a promising TE material because of light weight, high abundance of its constituent elements and high thermoelectric properties around 873 K (figure of merit, ZT= 0.96). For these reasons, Mg_2Si is expected to apply the component of automobile. However, Mg_2Si presents brittle failure behavior and it's fracture toughness is quite low (~0.64 $MPa \cdot m^{1/2}$, which is smaller than that of typical structural material). Therefore, it is necessary to improve fracture toughness. Particle dispersed strengthening is a prospective way to improve fracture toughness of brittle materials because the secondary phase dispersed intergranular or intergranular restrain crack propagation. However, the reinforcement dispersed matrix grain boundaries has negative influence on thermoelectric properties. In this study, intragranular-composites prepared by melting process to improve fracture toughness without reducing thermoelectric properties.
Pre-synthesized all-molten commercially available polycrystalline Mg_2Si-Sb 0.5 at. %- Zn 1.0 at. % was used as a starting material. Mg_2Si ingots were pulverized to powder with sizes of less than 25 µm. In addition, the powders were mixed with silicon carbide (SiC) nanoparticles. The volume fraction of SiC was set to be 1-10vol%. The powder mixtures were pressed under uniaxial pressure and packed by Mo foil. Then, the pressed samples were sealed in a quartz tube which was filled with argon gas. In addition, the compacted samples were heated at 1358 K for 5 min. Melted samples were pulverized to powder with sizes of less than 25 µm. Then, the powders were sintered by plasma activated sintering (PAS).
Young's modulus and fracture toughness of the sintered pellets were measured by ultrasonic pulse method and indentation fracture (IF) method. Electrical conductivity, Seebeck coefficient and Thermal conductivity were also measured by four-terminal sensing, thermo-electromotive force method and laser flash method. Dimensionless figure of merit (ZT) was determined using those values.
We successfully incorporate SiC nanoparticles within Mg_2Si grains through melting treatment. Fracture toughness of intragranular-composites increases about 80% compared with pure Mg_2Si-Sb 0.5 at. %- Zn 1.0 at. %. In contrast, TE properties are decreased with increasing volume fraction of SiC nanoparticles. However, we could confirm the effect of SiC nanoparticles dispersed within Mg_2Si grains, because electrical conductivity of intragranular-composites is higher than that of intergranular composites. In this presentation, the influence of SiC nanoparticles dispersed Mg_2Si grains on mechanical thermoelectric properties will be discussed.

PM06.05.39
The Effect of Vibration on Mechanical and Electrical Properties of Magnesium Silicide Based Thermoelectric Modules <u>Tetsuro Takagi</u>, Keisuke Nagayoshi, Takashi Nakamura, Ryo Inoue, Tsutomu Iida and Yasuo Kogo; Tokyo University of Science, Tokyo, Japan.

Magnesium-based silicide (Mg_2Si) is one of the most attractive materials for application in thermoelectric generators (TEG) because this material has high power generation efficiency at 300–600 °C. TE modules are typically composed of n-type and p-type TE leg, however difference of thermal expansion between p-type and n-type TE leg becomes critical problem. For fabrication of the Uni-leg TE modules composed of Mg_2Si, silver-alloy braze was used for bonding between legs and the metal terminals. In this case, nucleation of crack owing to thermal expansion mismatch of constituent materials is inevitable. Recent studies used aluminum as a bonding layer instead of silver-alloy braze because of its low melting point. These TE modules are usually subjected to thermal cycling and continuous vibration during operation, however, effects of vibration on mechanical, and electrical properties of TE modules have not been sufficiently investigated. For designing reliable TE module, it is necessary to understand mechanical properties of the interface and degradation of interface properties by vibration. The objective of this study is to develop TE modules fabricated by Al foil. Furthermore, evaluation of interface properties was done before and after vibration tests.
Polycrystalline Mg_2Si-Sb 0.5 at. %- Zn 1.0 at. % with particle size 25-75 µm was used as raw material. The Mg_2Si powder was sintered by plasma activated sintering (PAS). The Ni foils and the Mg_2Si pellet were bonded by PAS at 923 K under a pressure of 10 MPa in Ar atmosphere for 10 min. The Ni/Mg_2Si TE leg and the Ni terminal were bonded by hot pressing using the aluminum foil. The microstructure and phase composition of the prepared

samples were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The shear strength of the interface between Al/Ni before and after vibration test was measured by bonding tester PTR1101 with a displacement rate of 0.1 mm/min. The vibration test was also performed under the condition of 33, 200, 400 Hz frequency for 4 h by simple harmonic motion parallel to the interface using electrodynamic vibration test system ai210/SA1M.   Finite element (FE) analysis was also done to calculate natural frequencies and stress/strain distribution in TE modules during vibration.

$Mg_6Si_7Ni_{16}$ (η-phase) is formed between Ni electrode and Mg_2Si after hot pressing. Two phases were formed at the Ni/Al interface. Based on the results of microstructural analysis, evaluation of mechanical properties, and numerical simulation, the effect of simple harmonic motion parallel to the interface on performance of TE modules will be discussed.

8:30 AM *PM06.06.01
Deformation of a Pt-Vontaining RuAl Alloy Tapash Nandy[2], K.V. Vamsi[1], S. Karthikeyan[1], Tresa Pollock[3] and <u>Dipankar Banerjee</u>[1]; [1]Materials Engineering, Indian Institute of Science, Bangalore, India; [2]Defence Metallurgical Research Laboratory, Hyderabad, India; [3]Materials, University of California, Santa Barbara, Santa Barbara, California, United States.

We explore deformation structures arising from room temperature compressive deformation of polycrystalline Pt modified RuAl alloy. Intermetallics such as NiAl and CoTi that possess high melting points deform by <100> slip at room temperature while B2 phases such as CuZn and FeAl with relatively lower melting points or order-disorder temperatures deform by <111> slip. RuAl, although it has relatively high melting point, occupies a unique position in this hierarchy in that slip occurs by both <100> and <111> dislocations with debris of sessile <110> dislocations and complex dipole structures. <100> dislocations are cusped and cross slip frequently. <111> dislocations trail dipoles and also decompose into sessile configurations of <110>+ <100> dislocations in near screw orientations. An analysis of gamma surfaces in RuAl and the energetics of dislocation dissociations provides insight into its deformation behaviour.

9:00 AM PM06.06.02
Diversity and Phase Equilibria in Highly-Ordered η-Fe_2Al_5 Derivative Phases <u>Kodai Niitsu</u>[1, 2], Ryutaro Sakai[1], Masaya Higashi[1] and Haruyuki Inui[1, 2]; [1]Kyoto University, Kyoto City, Japan; [2]ESISM, Kyoto, Japan.

While being one of the most fundamental and practically important binary systems, Fe-Al binary system still has intriguing issues on its constituting phases and phase equilibria. The orthorhombic η-Fe_2Al_5 (space group *Cmcm*) is such an intermetallic compound, raising inconsistencies in its crystal structure and ordering tendency. To date, several derivatives with highly-ordered crystal structures such as η', η'', η''' and η^m phases have been reported to exist with slightly deviated stoichiometry from that of the η-Fe_2Al_5 phase. While various attempts have been demonstrated by means of transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and differential scanning calorimetry, some controversial remains on their crystal structures and the phase equilibria among these phases.
In this study, we fabricated various Fe-Al alloy ingots with Al content of 68–74 at.% and homogenized at various temperatures. TEM and scanning transmission electron microscopy (STEM) observations were performed on the thin foils prepared by electro-polishing. To refine the crystal structures, XRD was alternatively performed on the single crystals of some homogenized alloys.
As a result of systematic TEM and STEM observations, four kinds of highly-ordered intermetallic compounds (termed as η', η'', η''' and η^m in line with previous reports) are observed in addition to the η phase. These compounds have different ordering tendencies with maintaining the framework of the η phase, thus that their stoichiometry is slightly different from each other. In addition, periodic anti-phase boundaries (APBs) are observed in some of the compounds, which are presumably introduced to compensate for the lattice mismatch among the adjacent compounds. In spite of strong similarity in crystal structures, their phase stabilities show a remarkable contrast; the η'' and η''' phases seem to be stable up to ~1300 K with the solubility range of ~1 at.% but the η' and η^m phases exist only below ~650 K with little solubility range. This contrast may be attributed to the hierarchical ordering among these structures. The conclusive phase diagram will be also shown in the presentation.

9:15 AM PM06.06.03
Creep Mechanism of Lamellar Fe-Al Alloys Anke Schmitt[1], Sharvan Kumar[2], Alexander Kauffmann[1] and <u>Martin Heilmaier</u>[1]; [1]Karlsruhe Institute of Technology, Karlsruhe, Germany; [2]Brown University, Providence, Rhode Island, United States.

Iron aluminides are possible alternatives for steels in warm-temperature application due to their low-density and oxidation-resistance. However, their frequent use is limited mainly due to a low ductility at room temperature and rather poor creep resistance at elevated temperatures beyond 600°C. In order to improve the creep resistance of B2-ordered FeAl classical physical metallurgy approaches are used, such as solution strengthening, precipitation strengthening and dispersion strengthening. As previously demonstrated for TiAl, a lamellar microstructure can enhance the creep resistance as well. In the Fe-Al system, a lamellar microstructure can be obtained by an eutectoid transformation in the composition range of 55 – 65 at.% Al. Particularly, the high-temperature ε-phase, Fe_5Al_8 decomposes into B2-ordered FeAl and triclinic $FeAl_2$. The creep resistance of such a lamellar alloy was previously studied a constant true stress of 100 MPa and 700°C in compression. It exhibits a characteristic minimum after achieving a strain of roughly 0,5 %, which is followed by an increase of the creep rate with increasing time and strain. The absence of a pronounced steady-state regime is attributed to a deterioration of the lamellar structure in the vicinity of colony boundaries. The determined stress exponent indicates a creep based on dislocations motion. Nevertheless, the presence of the two phases combined with a high interphase density due to the lamellar morphology precluded final understanding of the individual contributions to the observed creep response – both, in the early stages as well as at and just beyond the minimum creep rate. Thus, TEM investigations of crept eutectoid FeAl material were performed on samples that were isothermally crept under above conditions and interrupted for microstructure analysis at characteristic strains. In this presentation we will discuss the following situations determining the strain rate response of the lamellar materials: a) Both phases contribute to the creep deformation from the beginning and the degradation of the lamellar morphology is responsible for the increase of the strain rate beyond the minimum. b) Only one of the two phases deforms and the second phase does not contribute directly to creep throughout the entire experiment, and the degradation of the lamellae causes the increase of the strain rate beyond the minimum. c) The second phase starts to creep-deform beyond the minimum causing the increase in the strain rate and subsequently, lamellae degradation enters the picture as well.

9:30 AM PM06.06.04

Understanding Structural Phase Transitions Between the Simpler Structures and Topologically Close-Packed Phases <u>Anirudh Raju Natarajan</u> and Anton Van der Ven; University of California, Santa Barbara, Santa Barbara, California, United States.

Structural phase transitions between vastly different crystal structures are often exploited to enhance the properties of structural and functional materials. Understanding the transformation mechanism in applications such as shape-memory, magnetocaloric, high-entropy and precipitation strengthened alloys is thus critical to developing better alloy chemistries. However, very few links between disparate structure classes are known. Further, such phase transitions typically involve several length-scales, making it difficult to develop rigorous ab-initio mesoscale models. In this talk, we will describe a new facile pathway connecting the simpler structures to a hierarchy of topological close-packed phases consisting of Kagomé nets and triangular layers. Several common intermetallic compounds such as the Laves phases are specific members of this family of structures. First-principles calculations reveal that the transformation pathways are primarily driven by a triangular to Kagomé transition that reduces the overcrowding of atoms. We will also describe how electronic structure methods may be coupled with statistical mechanics tools to develop rigorous mesoscale models that describe precipitate formation. The transition pathways and modeling methods presented here are expected to unlock novel design routes to either encourage (or suppress) the formation of such topologically close-packed phases in several metallic, polymeric, and colloidal systems.

9:45 AM PM06.06.05
Ultrahigh Elastically Compressible Intermetallic Compound, $CaKFe_4As_4$ <u>Gyuho Song</u>[1], Vladislav Borisov[2], William Meier[3], Keith Dusoe[1], John T. Sypek[1], Roser Valentí[2], Paul Canfield[3] and Seok-Woo Lee[1]; [1]University of Connecticut, Storrs, Connecticut, United States; [2]Theoretical Physics, Goethe University, Frankfurt am Main, Germany; [3]Physics and Astronomy, Iowa State University, Ames, Iowa, United States.

Intermetallic compounds often exhibit superior physical and chemical properties due to their unique atomic arrangements and crystal structures, but their practical applications have been significantly limited because most intermetallic compounds are extremely brittle and are not able to absorb strain energy high enough to sustain its structure. The nature of strong covalent bonds and complexity of crystal structures usually do not permit the plastic deformation, so brittle failure occurs at the elastic limit even less than 0.5% except a few limited materials such as shape memory intermetallic compounds. Therefore, it is extremely rare to obtain a large amount of elastic deformation over 10% in intermetallic compounds.

However, $CaKFe_4As_4$ recently began to receive great attention due to its superelasticity and potential usage of high temperature superconductivity. These two super-properties do not typically get along because superconductors, which are brittle oxides or intermetallic compounds in many cases, shatter easily particularly under non-hydrostatic stress state. Here, by synthesizing a single crystalline $CaKFe_4As_4$ through Sn-flux solution growth and performing *in-situ* micromechanical experiments, we report that the giant compressible strain, 13~17%, is possible under uni-axial compression along c-axis. Notably, this material is able to absorb the strain energy orders of magnitude higher than advanced engineering materials. The density functional theory shows that this unusually large elastic axial compressibility results from the half-collapsed tetragonal phase transition, which is induced by As-As atomic bond formation and magnetic moment collapse, and significant local compliance. All these processes are fully reversible upon unloading. Also, we performed in-situ cryogenic micromechanical test with liquid nitrogen cooling capability, and confirmed that superconductivity could be suppressed by inducing the half collapsed tetragonal around 1 GPa. This huge uni-axial reversible deformation mechanism is differentiated from the conventional shear mechanism, martensite-austenite phase transformation of shape memory intermetallic compounds and can be extended to over 1000 AX_2Y_2- and ABX_4Y_4-structured intermetallic compounds. Furthermore, this giant elastic strain could make strain engineering possible, leading to the development of mechanically-switchable functional materials, for instance, superconductivity switching even under uni-axial mechanical loading, which is significantly desirable for device applications.

10:00 AM BREAK

10:30 AM *PM06.06.06
Predicting Defect Behavior in Intermetallic Compounds by Merging *Ab Initio* Modeling and Machine Learning <u>Mark Asta</u>[1,2], Bharat Medasani[3], Hong Ding[2], Wei Chen[4], Kristin Persson[1,2], Andrew Canning[1], Maciej Haranczyk[1] and Anthony Gamst[5]; [1]Lawrence Berkeley National Laboratory, Berkeley, California, United States; [2]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; [3]Pacific Northwest National Laboratory, Richard, Washington, United States; [4]Illinois Institute of Technology, Chicago, Illinois, United States; [5]University of California, San Diego, California, United States.

We present a combination of machine learning and high throughput calculations to predict point defect behavior in binary intermetallic (A–B) compounds, using as an example systems with the cubic B2 crystal structure (with equiatomic AB stoichiometry). High throughput first principles density functional calculations have been employed to compute intrinsic point defect energies in 100 B2 intermetallic compounds. The systems are classified into two groups: (i) those for which the intrinsic defects are antisites for both A and B rich compositions, and (ii) those for which vacancies are the dominant defect for either or both composition ranges. The data was analyzed by machine learning-techniques using decision tree, and full and reduced multiple additive regression tree (MART) models. Among these three schemes, a reduced MART (r-MART) model using six descriptors presents the highest fit and predictive accuracy. This model is used to predict the defect behavior of other B2 compounds, and it is found that 45 % of the compounds considered feature vacancies as dominant defects for either A or B rich compositions (or both). The ability to predict dominant defect types is important for the modeling of thermodynamic and kinetic properties of intermetallic compounds, and the present results illustrate how this information can be derived using modern tools combining high throughput calculations and data analytics. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231: Materials Project program KC23MP.

11:00 AM PM06.06.07
Design of a Hardenable Cu-Cr-Nb Alloy by Laser Metal Deposition <u>Anoop R. Kini</u>[1], Dora Maischner[2], Andreas Weisheit[2], Eric Jägle[2] and Dierk R. Raabe[1]; [1]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany; [2]Fraunhofer Institute für Lasertechnik, Aachen, Germany.

Dilute copper alloys are of high interest, positioned uniquely at the intersection of the property combination, specifically conductivity (thermal/electrical) and mechanical strength (hardness). We propose the design of a dilute Cu-Cr-Nb alloy focusing on achievement of greater hardening (146 VHN), compared to respective established ternary alloys. We achieve this goal, by processing the alloy by laser metal deposition (LMD). Importantly, we utilize a lower alloying solute amount (4 at.%; lower by at least ~ 33%) compared to previous alloys. Careful alloy compositional choice results in introduction of novel hardening contribution in this ternary system, by coherency of precipitates enriched in chromium. The precipitate coherency, size and chemical composition has been investigated by transmission electron microscopy and atom probe tomography. The coherency hardening operates in conjunction with dispersed Laves phase particle hardening. Each of the contributions has been modelled, which adds up to match the measured hardness of 146 VHN. Spatial homogeneity of hardening has been established by means of nano-indentations across the alloy sample. The hardening attained is in the as-produced condition itself i.e. after LMD. This is because of favorable LMD processing conditions for in-situ precipitation (intrinsic heat treatment).

11:15 AM PM06.06.08

A New A*b Initio* Modeling Scheme for Ion Self-Diffusion Coefficient Applied to ε-Cu₃Sn Phase of Cu-Sn Alloy <u>Tom Ichibha</u>[1], Genki Prayogo[2], Kenta Hongo[3, 4, 5] and Ryo Maezono[1]; [1]School of Information Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; [2]School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; [3]Research Center for Advanced Computing Infrastructure, Japan Advanced Institute of Science and Technology, Nomi, Japan; [4]PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Japan; [5]Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan.

Ion diffusion via vacancy relates to various properties such as corrosion, monotectoid, fracture, and degradation in material solids. To reveal the microscopic processes of ion diffusion, *ab initio* simulations have been used commonly. On the other hand, when evaluating self-diffusion coefficient, its application has been limited in just simplest systems, because it is difficult to model diffusion coefficients based on predictable quantities especially for complicated structures such as long-range periodic crystals.

We tackled this issue with our own idea in order to simplify the complicated connection of ion sites based on the calculated barrier energies. We established a modeling scheme, introducing a couple of novel concepts, "domain division" and "coarse graining" of the diffusion network: The first concept is expected to be useful for long-lange periodic structures: We classify the diffusion routes into three groups 1-3, according to their barrier energies, $E_1 < E_2 < E_3$. The diffusion routes in group III can be excluded from the diffusion network, because an ion jump affects the diffusion coefficient by the Boltzmann factor of barrier energy. Then, if the diffusion network is (fortunately) separated into a few types of disjunct domains, the problem is reduced into multiple modelings for each domain. These modeling are further simplified with the second concept. Since vacancies can move along the diffusion routes in group 1 more frequently than those in group 2, ion sites connected by these routes can be replaced with just a single site. Then, the diffusion networks of each domain are course-grained with the representative sites to be simplified.

We applied the modeling scheme to evaluate the diffusion coefficient of Cu ion in ε-Cu₃Sn alloy, which is a typical system having long-range periodicity. The predicted diffusion coefficients agree with experimental values, and it is better than those reported by a classical molecular dynamics by a digit. Furthermore, we justified the constructed model by comparing the correlation factor with that of two-dimensional hexagonal lattice at high temperature limit.

11:30 AM PM06.06.09

Solidification Microstructure of Ti-Ag and Ti-Ag-Nb Immiscible Alloys Focusing on the Formation of Intermetallic Compounds <u>Takeshi Nagase</u>; Osaka University, Ibaraki, Japan.

Ti-Ag alloy system is characterized by a flat liquidus line and the existence of two intermetallic compounds (TiAg and Ti₂Ag) in the binary phase diagram. The solidification microstructure of binary Ti-Ag alloys and ternary Ti-Ag-Nb alloys were investigated focusing on the formation of intermetallic compounds. In binary Ti₆₆.₇Ag₃₃.₃ alloy, the conventionally cast ingots obtained by arc melting technique showed a dendritic structure that included Ti-Ag-based intermetallic compounds; on the other hand, the rapidly solidified melt-spun ribbons showed a particulate microstructure comprising Ag-rich globules and a Ti-rich matrix phase without Ti-Ag-based intermetallic compounds. The formation of emulsion-like structures in the rapidly solidified specimens can be explained in terms of liquid phase separation [1]. The occurrence of the liquid phase separation also can be seen in Ti-Nb-Ag alloy [2].
References
[1] T. Nagase, M. Matsumoto, Y. Fujii, Journal of Alloys and Compounds, 738, 440-447 (2018)., "Microstructure of Ti-Ag immiscible alloys with metastable liquid phase separation", https://doi.org/10.1016/j.jallcom.2017.12.1388
[2] T. Nagase, M. Matsumoto, Y. Fujii, Microscopy, 66 S1, i22 (2017)., "Microstructure of Ti-Nb-Ag immiscible alloys with liquid phase separation", https://doi.org/10.1093/jmicro/dfx064

11:45 AM PM06.06.10

Microstructure-Corrosion Property Correlation in Graphene Oxide Containing SnZn and SnNi Composite Coatings <u>Rekha Mahendrakar</u>; Indian Institute of Science, Bangalore, India.

Coatings have been traditionally used for protecting the underlying substrate against corrosion. Recently, it has been demonstrated that chemical inertness and impermeability of graphene/graphene oxide (GO) makes them excellent coating material for corrosion protection. Use of only graphene/GO as coating material is however impractical due to challenges associated with large scale production of large area graphene/GO sheet with minimal defects at low cost. One other way to employ these materials for corrosion protection is by incorporating them into the matrix of conventional coatings. Researchers have shown that composite metallic coatings containing graphene/GO exhibit higher corrosion resistant than corresponding pristine metallic coatings. This work explores the correlation between microstructure and electrochemical behaviour of SnZn-GO and SnNi-GO composite coatings electrodeposited on mild steel substrate. Amount of GO in the composite coatings was varied by changing the concentration of the chemically synthesized GO in the electrolyte bath. Corrosion behaviour of the SnZn and SnNi coatings were examined through potentiodynamic polarization and electrochemical impedance spectroscopy methods. Transmission electron microscopy technique was used to investigate the coating microstructure. In the case of SnZn-GO composite coating, relative compactness of the coatings increased with increase in the concentration of GO. Texture and the crystallite size, however, did not show any significant variation with the concentration of GO in the coatings. Microstructural investigation of the coating cross-section revealed large scale segregation of Zn-rich and Sn-rich phases in pure SnZn coating. However, in the case of SnZn-GO composite coatings uniform distribution of Zn phase in Sn-rich matrix was observed. This distribution caused early and uniform formation of ZnO, which is the corrosion product, yielding better corrosion resistance for the SnZn-GO composite coatings as compared to pure SnZn coating. In the case of SnNi-GO composite coating, morphological characterization revealed the presence of rod shaped features in a flat matrix. Structural characterization showed presence of Sn-rich phase along with Ni₃Sn₄, Ni₃Sn₂ and Ni₃Sn intermetallics. Crystallite size of the Sn-rich phase decreased significantly due to the addition of GO. Microstructural investigation revealed that the SnNi coating without GO contained Sn and Sn-Ni solid solution grains. Whereas, SnNi coatings with GO contained Sn grains with Ni present at the grain boundaries. With increase in the GO content in the SnNi-GO composite coatings, size of the Sn sub-grains within the larger Sn grains reduced. Smaller Sn sub-grains and presence of Ni at the grain boundaries facilitated formation of the oxide corrosion products which provided protective cover and enhanced the corrosion resistance behaviour for the composite coating.

SESSION PM06.07: Intermetallic Precipitates
Session Chairs: Anne Denquin and Dierk Raabe
Wednesday Afternoon, November 28, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.07.01
Grain Boundary Segregation and Transformation in Complex Alloys <u>Dierk R. Raabe</u>, A. Kwiatkowski da Silva, D. Ponge, Z. Li, S. Makineni, L. Li and Baptiste Gault; Max Planck Institute for Iron Research, Duesseldorf, Germany.

We report about recent findings which reveal the close connection and interdependence among Fowler-Guggenheim-type equilibrium segregation, local spinodal decomposition and phase transformation phenomena at lattice defects. We show that several types of phase formation effects at grain boundaries and dislocations can be jointly understood in terms of preceding equilibrium segregation and decomposition precursor states. Random high angle grain boundary structure features seem to be of secondary relevance for these phenomena owing to prevalence of the local chemical driving forces. Corresponding examples which have been documented by applying site-specific correlative atom probe tomography and electron microscopy probing are given for Fe-Mn model steels [1-3], superalloys and high entropy alloys [4].

[1] A. Kwiatkowski da Silva, G. Leyson, M. Kuzmina, D. Ponge, M. Herbig, S. Sandloebes, B. Gault, J. Neugebauer, D. Raabe, Confined chemical and structural states at dislocations in Fe-9wt%Mn steels: A correlative TEM-atom probe study combined with multiscale modelling (2017) Acta Materialia, 124, 305-315.
[2] A. Kwiatkowski da Silva, D. Ponge, Z. Peng, G. Inden, Y. Lu, A. Breen, B. Gault, D. Raabe, Phase nucleation through confined spinodal fluctuations at crystal defects evidenced in Fe-Mn alloys (2018) Nature Communications 9, 1137.
[3] M. Kuzmina, M. Herbig, D. Ponge, S. Sandlöbes, D. Raabe, Linear complexions: Confined chemical and structural states at dislocations (2015) Science 349, 1080-1083.
[4] Z. Li, K. G. Pradeep, Y. Deng, D. Raabe, C. C. Tasan, Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off (2016) Nature 534, 227–230.

2:00 PM PM06.07.02
Effects of Si on Phase Stability and Precipitation Behavior of C14 Laves Phase (Fe,Cr)$_2$(Nb,Mo) in High Cr αFe-base Alloys <u>Yoshisato Kimura</u>, Ko Kato and Yaw Wang Chai; Tokyo Institute of Technology, Yokohama, Japan.

Ferritic stainless steels with high Cr contents around 20 at% can be used not only for heat resistant alloys such as exhaust manifolds of automobile engines but also for functional alloys such as separator or/and interconnector of fuel cells. It is important to control microstructure of ferritic stainless steels focusing on morphology of C14 Laves phase precipitates depending on applications. Structural applications tend to require fine and homogeneous distribution of C14 Laves phase, while gradient distribution with rather large volume fraction would be desirable for functional applications mentioned above. The objectives of the present work are to understand effects of the Si addition on phase stability and precipitation behavior of C14 Laves phase (Fe,Cr)$_2$(Nb,Mo) in the Fe-Cr-Nb-Mo quaternary αFe-base model alloys, and to determine the growth mechanism of C14 Laves phase in the bcc αFe matrix.
It is interesting that the addition of Si remarkably enhances the precipitation of C14 Laves phase cooperatively with Mo. For instance, the volume fraction of C14 Laves phase increases about twice as large in an Fe-20Cr-0.5Nb-2Mo alloy (in at%) by the addition of 2 at% Si compared with Si-free counterpart under the same aging condition at 1073 K for 24 hours. Contrary to this, the addition of Si is not effective to increase the volume fraction of C14 Laves phase on a Mo-free Fe-20Cr-0.5Nb alloy. It is suggested that the addition of Si improves the phase stability of C14 Laves phase while the partitioning of Mo into C14 Laves phase would be promoted due to the attractive interaction between Mo and Si. It is noteworthy that the site preference of Si in binary C14 Laves phase, Fe$_2$Nb and Fe$_2$Mo, was examined using the electron probe microanalysis. It was found that Si substitutes for the both-site in Fe$_2$Nb, and for the Fe-site in Fe$_2$Mo. The lattice mismatch between the bcc αFe matrix and C14 Laves phase decreases as the Mo content increases, which may lead to the uniform distribution of fine Laves phase precipitates. We have also determined that the growth mechanism of C14 Laves phase in the bcc αFe matrix is the ledge mechanism in an Fe-20Cr-0.5Nb-1Mo alloy annealed at 1073 K for 24 hours, using the transmission electron microscopy. The terrace is formed on the close-packed basal plane of hcp C14 structure as we predicted. Precipitation particles tend to grow in a needle-like shape depending on the anisotropic difference of lattice mismatch. The addition of Si up to 2 at% on Fe-20Cr-0.5Nb-1Mo alloys seems not to have appreciable effect on the ledge mechanism of C14 Laves phase precipitates.

2:15 PM PM06.07.03
Role of Cr-rich Carbide Precipitates in the Intergranular Oxidation of Ni-Cr Alloys <u>Maria Sushko</u>, Daniel Schreiber, Kevin Rosso and Stephen Bruemmer; Pacific Northwest National Laboratory, Richland, Washington, United States.

The influence of grain boundary Cr carbides on the intergranular (IG) oxidation behavior of a Ni-16Cr alloy is considered using a novel atomistic-to-mesoscale model and three-dimensional atom probe tomography (APT). The results show that Cr carbide strongly perturbs the collective reactive dynamics of oxidizing species and alloy elements in the IG region. Strong attractive interactions between oxygen and carbide create a driving force for Cr and Ni accumulation in the grain boundary adjacent to the carbide, and for the depletion of Cr and Ni ahead of the oxidation front beyond the carbide. High local Cr chemical potentials from Cr carbide and Cr in the alloy dictate preferential oxidation of Cr and the formation of Cr$_2$O$_3$ in the region adjacent to the carbide 1-2 nm away from the carbide surface. APT observations also reveal Ni accumulation at the interface between the carbide and Cr$_2$O$_3$, possibly indicating emergence of a distinct interfacial phase. The results inform a mechanistic model underlying the thermodynamics of IG oxidation of a Ni-Cr alloy in the presence of Cr carbide, and shed light on the mechanism of carbide-assisted protection of the alloy against grain boundary corrosion/oxidation. Our findings can be used for the development of new alloys that are more stable under extreme conditions.

2:30 PM BREAK

3:30 PM *PM06.07.04
AlTiNbVX (with X= Mo or Ta) Refractory High Entropy Alloys for Aeroengines Applications <u>Anne Denquin</u>, Zhao Huvelin and Antoine Lacour-Gogny-Goubert; ONERA, Châtillon, France.

Materials research has been for long a major contributor to the improvement of turbine engines, and particularly driven in the last decades by the quest of lightweight substitutes to nickel-based superalloys. As these superalloys exhibit only small space for further improvements, the engine manufacturers have spent their efforts in developing lightweight solutions, like intermetallics or Ceramic Matrix Composite. A new class of metallic materials, called "High Entropy Alloys" (HEAs) seems to be a promising way toward the development of new and innovative metallurgy, especially in the framework of turbomachine applications for which the research and development of materials with better durability under various constraints is essential. Two groups of HEAs can be identified for use at high temperatures: (i) HEAs based on the 3d-transition metals (Co, Cr, Cu, Fe, Mn, Ni, Ti, and V); and (ii) HEAs based on refractory elements, which are called refractory high entropy alloys (RHEAs). This talk will focus on RHEAs : AlNbTiVX equiatomic compositions,

with X = Ta or Mo, have been studied in terms of microstructure, sensitivity to heat treatment and high temperature mechanical behaviour. The alloying effect of aluminium on the microstructure, phase evolution and mechanical properties of the AlNbTiVMo system were also investigated. The results will be discussed in terms of potential of these alloys for high temperature applications.

4:00 PM PM06.07.05
Microstructure and Strength of Heat-Resistant Aluminum Alloy Strengthened by T-Al$_6$Mg$_{11}$Zn$_{11}$ Intermetallic Phase Naoki Takata, Masato Ishihara, Satoshi Nakatsuka, Asuka Suzuki and Makoto Kobashi; Nagoya University, Nagoya, Japan.

Wrought aluminum (Al) alloys with relatively high specific strength are widely used for radial compressor impellers in vehicle turbochargers. The limited high-temperature strength determines the service temperature of compressor impellers for turbochargers. One of the common wrought Al alloys used for radial compressors is alloy 2618. However, its strength is significantly reduced at temperatures above 200°C. Thus, further improving the combustion efficiency at elevated temperatures make it necessary to increase the service temperature of the Al alloys applied for the radial compressor impellers. In the present study, we designed an aluminum (Al)-based alloy with α-Al (fcc) matrix strengthened by T-Al$_6$Mg$_{11}$Zn$_{11}$ (cubic) intermetallic phases using a large two-phase region of α and T phases in the Al–Mg–Zn ternary system for the possible application of the radial compressor impellers operating at elevated temperatures above 200°C. Thermodynamic assessments revealed a composition of Al–5Mg–3.5Zn (at%) with the α-Al phase reinforced with high fractions (approximately 10 %) of T phase. We attempted to control microstructure of the Al–5Mg–3.5Zn alloy by the solution treatment and subsequently aging. T phase preferentially precipitates on grain boundaries in the α-Al matrix, which increases the area fraction of T phase on grain boundaries during the aging. The granular precipitates of T phase were dispersed rather homogenously in theα-Al matrix with a particular orientation relationship of $(1-11)_\alpha$ // $(1-21)_T$ and $[011]_\alpha$ // $[111]_T$ at elevated temperatures above 300°C. During the aging at 200°C there were numerous fine precipitates with a mean size of approximately 20 nm in grain interior, which is likely the metastable phase associated with T phase. The present alloy aged at 200°C for 1 h exhibits high yield strength of approximately 260 MPa at 200°C, which is much superior to those of the conventional Al alloys at an elevated temperature corresponding to possible service temperatures for the compressor impellers in turbochargers.

4:15 PM PM06.07.06
The Role of Intermetallic Particles on the Bendability of AA6xxx Alloys Sin Ting Cynthia Chang[1], Miroslav Smid[1], Samy Hocine[1,2] and Helena Van Swygenhoven-Moens[1,2]; [1]Photons for Engineering and Manufacturing Group, Paul Scherrer Institut, Villigen, Switzerland; [2]Neutrons and X-rays for Mechanics of Materials, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The role of intermetallic particles on the bendability of Al 6xxx alloys is investigated during in-situ bending tests in a scanning electron microscope (SEM). High resolution digital image correlation (HR-DIC) analysis is undertaken to investigate the role of microstructural features on the strain partitioning and the role of pre-existing voids and precipitates on early stages of the crack initiation and fracture. Aluminum alloys AA6014 and AA6016 after T4 temper, i.e. after solution heat treatment and quenching are investigated in as-received and pre-strained (10 % tension) conditions. The in-situ bending setup was developed in-house and is based on a Kammrath & Weiss tensile module suitable for a scanning electron microscope (SEM) chamber. The experiments are performed with constant displacement rate and with several interruptions for SEM imaging at selected displacement values. DIC with high spatial resolution is performed using colloidal silica (OPS) particles. Full-field strain maps are complemented with Electron Backscatter Diffraction (EBSD) maps before and after the bending. The crystal orientation data enables the identification of activated slip planes observed by HR-DIC. Furthermore, EBSD data document the different texture evolution in the compression and tension parts of the specimen.
It is observed that the pre-existing voids and cracks along the intermetallics play an important role in the strain localization. At small bending, intermetallics can deform and become elongated in the tension direction. With further bending, strain localization is observed around intermetallics leading to cracking of intermetallics and producing additional voids in-between the intermetallics. Failure mechanisms are often related to the presence of fine precipitates along grain boundaries. The final crack leading to sample failure propagates along the cracked intermetallics. The results are discussed in terms of the different type of intermetallics present in AA6014 and AA6016.

4:30 PM PM06.07.07
Superior Mechanical Properties Induced by Extrusion in Mg-Based Long-Period Stacking Ordered (LPSO) Phase Alloys Koji Hagihara[1], Zixuan Li[1], Michiaki Yamasaki[2], Yoshihito Kawamura[2] and Takayoshi Nakano[1]; [1]Osaka University, Osaka, Japan; [2]Kumamoto University, Kumamoto, Japan.

The recent hot topic found in Mg-alloys containing large amount of long-period stacking ordered (LPSO) phase is the unusual increase in the strength by the extrusion. In this study, the detailed mechanisms which induce the drastic strengthening of the LPSO-phase alloys by extrusion was first elucidated on the basis of the quantitative analysis. To achieve this, the temperature and loading orientation dependence of the deformation behavior of the Mg$_{88}$Zn$_4$Y$_7$ extruded alloy which contains a ~86 vol.% of LPSO-phase were examined.
Using several extruded alloys with different extrusion ratio, the influence of extrusion ratio to the microstructure formation and the following mechanical properties were examined. Rectangular specimens were cut by electro-discharge machining from the as-cast ingot and extruded alloys, and the mechanical properties of them were examined by compression tests. The tests were conducted in a temperature range between the room temperature and 400 degree C in a vacuum. Two loading orientations were selected for the compression test; one is parallel to the extrusion direction (0 orientation), and the other is inclined at an angle of 45 degree from the extrusion direction (45 orientation), to clarify the anisotropic mechanical properties of the extruded alloys.
As a result, the yield stress of the LPSO phase alloy was found to exhibit a strong orientation dependence varied with the extrusion ratio. Especially, the yield stress of the extruded alloy with the reduction ratio of 10 showed an extremely high value more than 450MPa when loaded at 0 orientation, while it was largely reduced when loading at 45 orientation. This strong anisotropy of the plastic deformation behavior was considered to be derived from the variation in the deformation mechanisms depending on the loading orientation because of the development of strong {10-10} fiber texture along the extrusion direction. Basal slip was found to govern the deformation behavior at 45 orientation, while the predominate deformation mechanism varied from basal slip to the formation of deformation kink band at 0 orientation, as increasing in the extrusion ratio. In addition, it was found that the introduction the deformation kink band boundary during the extrusion process effectively act as strong obstacles against the motion of basal slip. This contributes to the drastic increase in the yield stress and work-hardening rate of the LPSO-phase alloys in the wide temperature range investigated.

4:45 PM PM06.07.08
Atomistic Simulation and Modeling of γ-Precipitate Nucleation in Mg-Al Alloys Peng Yi and Michael L. Falk; Johns Hopkins University, Baltimore, Maryland, United States.

Magnesium alloys have drawn increasing interest as a lightweight material for applications in transportation and aerospace industries. Some Mg-Rare earth alloys have shown significant precipitation hardening properties. These hardening properties are determined by the morphology and distribution of the precipitate particles, which strongly depend on the processing conditions during aging treatment, for example, temperature, applied strain, and the presence of defects like dislocations. It is important to understand how these processing conditions affect the precipitation process, particularly during the initial nucleation stage. This understanding is crucial for processing condition optimization, property prediction, and materials design for performance improvement and cost reduction.

We studied the nucleation of γ-$Mg_{17}Al_{12}$ precipitates in Mg-Al alloys with various solute Al concentrations, using atomistic simulation and modeling methods. The critical nucleus size at 277°C (550K) was determined using molecular dynamics simulations with a survival probability method. The critical nucleus size is very sensitive to the solute concentration; and is compared with calculations based on the chemical driving force and interfacial energy. The external pressure plays an important role in affecting the critical nucleus size as well. The external pressure not only changes the misfit strain energy, but also significantly changes the interfacial energy. As a result, although γ precipitate is denser than the a matrix, counter-intuitively nucleation is favored under tension conditions rather than compression conditions.

We also calculated the effect of dislocations on the nucleation of γ precipitate. The theoretical framework detailed in a number of reviews [1, 2] and first-principle calculation database were used for our thermodynamic modeling in calculating the nucleation rate of dislocation facilitated precipitation. The calculation results were used to compare with recent equal channel angular extrusion (ECAE) experiments of γ precipitation at 150°C (423K), where the dislocations are found to be preferable forming sites for the precipitates.

1. Russell, K.C., *Nucleation in solids: The induction and steady state effects.* Advances in Colloid and Interface Science, 1980. **13**(3): p. 205-318.
2. Christian, J.W., *The Theory of transformations in metals and alloys : an advanced textbook in physical metallurgy*. 2d ed. ed. 1975, Oxford ; New York.

SESSION PM06.08: Shape Memory Alloys
Session Chairs: Hideki Hosoda and Hiroyuki Yasuda
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 104

8:30 AM *PM06.08.01
Cyclic Deformation Behavior of NiTi for Medical Devices <u>Sharvan Kumar</u>[1], Zhiwei Ma[1] and Dhiraj Catoor[2]; [1]School of Engineering, Brown University, Providence, Rhode Island, United States; [2]Core Technologies, Corporate Science, Technology, and Clinical Affairs, Medtronic, Minneapolis, Minnesota, United States.

NiTi shape memory alloys (SMA) are used in the medical device industry for fabricating self-expandable stents, stent grafts and heart valve frames that can be implanted with minimally invasive techniques This material experiences a reversible stress-induced martensitic phase transformation from its parent austenite form (B2 austenite ↔ B19' martensite) that is accompanied by 6-8% recoverable strain. The stress for the reverse transformation (martensite to austenite) is lower than that for the forward transformation, resulting in a stress-strain hysteresis. The combination of device geometry, deployment practice and conditions that prevail in service makes evaluating and isolating factors that control the cyclic deformation response and fatigue failure as well as predicting high cycle fatigue life of these biomedical implants particularly challenging. In uniaxial tension, the austenite-to-martensite transformation progresses heterogeneously, leading to a complex distribution of strain whose local magnitudes differ from what is globally imposed. Thus, mechanistically interpreting the cyclic response of ultrafine ligaments that compose the stent construct in bending poses a significant scientific challenge. To address some of these issues, we have used a mildly center-tapered flat dog-bone specimen geometry that has been subjected to uniaxial tensile cyclic loading from the lower stress plateau where the material is in a mixed-phase state to mimic device service conditions. We apply controlled displacement amplitudes and obtain local strains experienced by the co-existing phases in the specimen gauge section using digital image correlation; we use a high-speed camera to monitor the specimen surface to track phase transformation and fracture initiation and propagation. We have examined the consequence of imposed cyclic frequency and testing medium on cyclic response. Additional experiments have been conducted to obtain fatigue life as a function of imposed displacement amplitude. The results from these experiments will be presented and their implications will be discussed.

9:00 AM PM06.08.02
Phase Transformation and Degradation of Superelastic NiTi During Uniaxial and Multiaxial Loading W-N. Hsu[1, 2], Miroslav Smid[2], Efthymios Polatidis[2], Steven Van Petegem[2] and <u>Helena Van Swygenhoven-Moens</u>[1, 2]; [1]NXMM-IMX-STI, Ecole Polytechnique Federale de Lausanne, Villigen, Switzerland; [2]PEM-LSC-PSD, Paul Scherrer Institute, Villigen, Switzerland.

The reversible deformation-induced martensitic transformation in NiTi gives rise to superelasticity. NiTi is used as structural material for stents in biomedical applications. The slender and intricate structure of a stent causes the material to experience locally multiaxial loading conditions. However, until now most of the knowledge on the martensitic transformation and the degradation mechanisms in NiTi is based on uniaxial loading experiments. The effect of multiaxial loading or changes in load path on the behavior of the material remains unclear.
The transformation behaviour of a commercial superelastic NiTi material is studied during uniaxial tension and load path changes by employing a novel miniaturized biaxial stage and cruciform shaped specimens [1]. The initial microstructure consists of large austenitic grains subdivided in bands of nanoscaled sub-grains [2]. Cruciform shaped samples are subjected to various loading conditions including uniaxial tension, equibiaxial tension and load paths that involve sudden changes in loading direction. The transformation behavior and martensitic variant selection is studied using insitu xray diffraction experiments carried out at the MS beamline of the Swiss Light Source and insitu HRDIC experiments carried out in an SEM. Microstructural characterization is complemented by EBSD analysis.
The results show a strong correlation of the martensitic transformation with Schmid's law during uniaxial loading. Bands of nanograins transform collectively and produce high-strain bands suggesting the importance of grain interactions at the nanoscale [2]. Evidence of non Schmid behavior is obtained by keeping some variants when going from an uniaxial stress to a multiaxial stress state. This affects the degradation mechanisms during load path changes. The footprints of material degradation after 100 load-unload cycles is visible in xray diffraction, interpreted and discussed in term s of the applied loading path.

[1] Experimental Mechanics 57 (2017) 569.
[2] Acta Materialia 144 (2018) 874

9:15 AM PM06.08.03
Scientific Understanding of Interfaces in Functional Materials <u>Huseyin Sehitoglu</u> and Sertan Alkan; University of Illinois, Urbana, Illinois, United

States.

Scientific studies of material interfaces are paramount to understanding the material performance. Despite the need to understand interfaces, most analyses and experiments in materials sciences and engineering have focused on bulk properties and homogenous idealizations bypassing the presence of interfaces. Such an idealized treatment is unable to capture the local stresses leading to irreversibilities and localization. We solve for the dislocation and disconnection networks at the interfaces. Then, we utilize a combination of Stroh formalism for anisotropic elasticity and molecular statics to gain insight into displacements at the dislocation cores which in turn are analyzed to formulate a Peierls-Nabarro stress. We develop a theory for rapid assessment encompassing material anisotropy, crystal lattice types, defect structures and local displacement fields. With such a formalism, the internal stress fields at interfaces are of critical importance for the flow CRSS (Critical Resolved Shear Stress) prediction. The CRSS show orientation dependence and significant non-Schmidt effects in NiTi shape memory alloy and show excellent agreement with experimental trends. The methodology is applicable to other functional materials.

9:30 AM PM06.08.04
Interfacial Energy and Geometry of Twin Boundary Between Martensite Variants in TiNi Shape Memory Alloy Takeshi Teramoto, Kazuya Nagahira and Katsushi Tanaka; Kobe University, Kobe, Japan.

A self-accommodation microstructure is martensitic microstructure of shape memory alloy. The self-accommodation microstructure is formed by martensitic transformation and constructed by the matensite variants. It is known that pairs of martensite variants forming twin are initially formed in the martensitic transformation. Based on the experimental results in TiNi shape memory alloy, this initial microstructure and included twin boundary show following two microstructural selectivity; 1. Pair of matensite variants have exact twin orientation relationship on the twin boundary (fully compatible interface) 2. Twin type of twin boundary is {-111} type I twin. To understand the selectivity of the initial stage martensitic microstructure in TiNi alloy, geometrically non-linear theory analysis is performed to reveal the geometry of fully compatible twin boundary. Then, the interfacial energy of fully compatible interface is analyzed by the first-principle calculation to reveal the selectivity of twin type.
The self-accommodation microstructure formed by B2-B19' martensitic transformation was adopted as an analysis model. The lattice parameters of B2 parent phase and B19' martensitic phase are a_{B2}=3.015Å, $a_{B19'}$=2.889Å, $b_{B19'}$=4.120Å, $c_{B19'}$=4.622Å and $\beta_{B19'}$=96.8° respectively. The first-principle calculation was performed using the Vienna Ab initio Simulation Package (VASP) code.
In B2-B19' martensitic transformation, there are 552 variant pairs in the combination logic. Fully compatible interface can be formed in the 96 variant pairs and, these variant pairs are classified into 4 groups. Except for these 4 groups, geometrically inevitable incompatibility arises in the microstructure during the formation and growth process. Fully compatible 4 groups are constructed by {100} compound twin (group A), {011} type I twin (group B), {-111} type I twin (group C) and {111} type I twin (group D) respectively and, group C is preferentially formed in the initial stage of martensitic transformation in the actual microstructure of TiNi alloy. Interfacial energy of these twin boundary was analyzed by first-principle calculation. Interfacial energy of group A, B, C and D are 64, 136, 67 and 108 (mJ/m$_2$) respectively. Because of the small volume of the initial microstructure, it is reasonable that twin boundary having small interfacial energy is preferentially formed in the initial stage of martensitic transformation. Group A and C show relatively low interfacial energy. This is one of the reasons that group C is preferentially formed in the initial stage of martensitic transformation.

9:45 AM PM06.08.05
Cyclic Properties of Superelasticity in Heusler-Type CuAlMnNi Alloys Nobuyasu Matsumoto, Ryosuke Kainuma and Toshihiro Omori; Engineering, Tohoku University, Sendai, Japan.

CuAlMn (CAM) alloy is one of the attractive shape memory alloys for practical applications because of high superelastic (SE) performance, high cold-workability and low cost. The SE properties of CAM alloy are known to be affected by relative grain size and the single-crystalline specimens show excellent properties [1]. Recently, our group has established the method for obtaining extremely large single-crystals in this alloy by cyclic heat treatment (CHT) without deformation process [2], and achieved to fabricate ultra-large single-crystalline rods of about 700 mm in length [3]. On the other hand, the most critical drawback for the practical use in this alloy is the low cyclic properties. Actually, in Cu-17Al-11.4Mn (at.%) alloy, the residual strain suddenly increases at about 100th cycle [4], while keeping a low value until 10^5 cycles in NiTi [5]. In this work, for the CuAlMnNi (CAMN) alloys, in which precipitation hardening by NiAl B2 phase is expected, the microstructures and the cyclic SE properties were examined.
CAMN single-crystalline sheets with dimension of 1×5×60 mm^3 were obtained by the CHT process as well as in the CAM alloys. In the CAMN sheet, excellent cyclic properties in SE with the residual strain smaller than 0.5% at 2000th cycle for applied strain of about 5 % were obtained. This dramatic improvement in cyclic properties is due to coherent precipitation of the NiAl phase.

References
[1] Y. Sutou et al., Acta Mater., 61 (2013) 3842-3850
[2] T. Omori et al., Science 341 (2013) 1500-1502
[3] T. Kusama et al., Nature Comm. 8 (2017) 354
[4] K.C. Shrestha et al., J. Mater. Civ. Eng. 28 (2016) 04015194
[5] J. Van Humbeeck et al., in Shape Memory Materials (ed. K. Otsuka et al.) 149-183

10:00 AM BREAK

10:30 AM *PM06.08.06
Ultra-Large Single Crystals by Abnormal Grain Growth in Cu-Al-Mn Heusler-Type Shape Memory Alloy Ryosuke Kainuma, Toshihiro Omori and Tomoe Kusama; Tohoku University, Sendai, Japan.

Intermetallic compounds are generally brittle, which is one of the main reasons to impede practical use. In 1996, we reported Cu-Al-Mn (CAM) shape memory alloy (SMA) with high ductility by decrease of degree of order in the parent phase with L2$_1$ ordered structure [1]. The superelastic (SE) property in SMA is affected by grain size [2] and single crystalline sample is known to show SE property better than polycrystalline one. Recently, we discovered a new rout to obtain an extremely large single crystal using abnormal grain growth only by cyclic heat treatment [3]. In this presentation, the alloy design for the high ductility and the excellent SE in the CAM SMA is reviewed and the microstructural control to obtain the ultra-large single crystal [4] is introduced.
(References)
[1] R. Kainuma et al., Metall. Mater. Trans. A, 27A (1996) 2187
[2] Y. Sutou et al., Acta Mater., 53 (2005) 4121
[3] T. Omori, et al., Science, 341 (2013)1500.
[4] T. Kusama et al. , Nature Comm., 8 (2017) 354.

11:00 AM PM06.08.07
Deformation Behavior of Stoichiometric Au₂CuAl Hideki Hosoda[1], Akira Umise[1, 2], Kenji Goto[1, 3] and Masaki Tahara[1]; [1]Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Japan; [2]Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Chiyoda-ku, Japan; [3] Tanaka Kikinzoku Kogyo K.K., Isehara, Japan.

Although TiNi becomes widely applied for biomedical applications, the possibility of Ni-hypersensitivity, weak X-ray radiography and artifact in magnetic resonance imaging are drawbacks. Then, in order to overcome these problem, we have proposed AuCuAl shape memory alloy especially for endovascular intervention. In the present study, the deformation behavior of the stoichiometric Au-25Cu-25Al (at.%) alloy is comprehensively summarized in addition to recent achievements by micro compression tests. It should be noted that the stoichiometric composition of β AuCuAl (Spangold) is recognized to be $Au_7Cu_5Al_4$, but in this study, we regard the stoichiometry as Au_2CuAl due to $L2_1$ Heusler of the parent phase. Mechanical tests used were indentation test, tensile test, compression test for polycrystal material as well as micro compression test for micro pillars. Micro Vickers hardness of Au_2CuAl is around HV170. By tensile tests at room temperature, the polycrystalline alloy specimens generally exhibit intergranular failure during elastic deformation. This brittleness is partially due to large grain size. The ultimate tensile strength is less than 100MPa. On the other hand by compression tests, the specimens show relatively good plastic deformation around 10% and the maximum stress is around 700MPa. By the micro compression tests, the single crystal specimens show clear shape memory and superelastic behavior. The stress for inducing martensite linearly increases with increasing test temperature and obeys the Clausius-Clapeyron type relationship. By taking into account of the observed slip plane during plastic deformation and the deformability of polycrystal, the dislocation slip is judged to be <111> type, instead of <110> and <100> types. This implies the polycrystalline materials must exhibit room temperature tensile deformability when the intergranular failure is suppressed, similar to B-added Ni_3Al. This work is supported by Grant-in-Aid for Scientific Research Kiban S 26220907 from Japan Society for the Promotion of Science.

11:15 AM PM06.08.08
The Effects of Defects and Microstructure on the Superelasticity of 1:2:2 Ternary Intermetallic Compounds Ian N. Bakst[1], Keith Dusoe[2], John Sypek[2], Seok-Woo Lee[2] and Christopher Weinberger[1]; [1]Colorado State University, Fort Collins, Colorado, United States; [2]University of Connecticut, Storrs, Connecticut, United States.

1:2:2-intermetallic compounds with the $ThCr_2Si_2$-type crystal structure have recently been shown to exhibit superelastic responses to hydrostatic, and *c*-axis uniaxial compression. It has been shown that the nature of this response can be altered through processing which is associated with the formation of point defects. In this talk, we combine materials theory and DFT to examine the role defects have on the mechanical response and phase stability of two compounds: $CaFe_2As_2$ and $LaRu_2P_2$. First, we explore the nature of isolated point defects in these materials. Then, we investigate the stability of high densities of these defects. We further investigate the responses of these defected structures using DFT, as well as how these structures, when combined with the pure compounds, alter the responses of these composites. These results are then compared against recent experiments, explaining the processing-microstructure-property relations of differently-fabricated samples. We are able to gain insight into the similarities and differences between two specific 1:2:2-intermetallics.

11:30 AM *PM06.08.09
Utilizing Shape Memory Alloys for Novel, Non-Pneumatic Tire Design Santo Padula and Colin Creager; NASA Glenn Research Center, Cleveland, Ohio, United States.

Conventional mobility elements, such as pneumatic tires, suffer from a number of issues related to reliability. Two of the more prevalent problems are the high likelihood of single point failure owing to puncture (i.e. flat tire), and loss of efficiency due to reduction in tire pressure over time. In order to overcome these limitations, alternative compliant tire designs not requiring pneumatics are being widely investigated. Although current designs have addressed some of the aforementioned issues, many of the designs tend to have their own set of limitations. First, most of the non-pneumatic tires designed for high load applications often have restricted envelopment capability, making their performance less than optimal, especially on uneven terrain. Second, many of the designs that can achieve larger envelopment capability tend to still suffer from large amounts of plasticity (permanent deformation) or failure (rupture). Both of these limitations are the direct result of the choice of material being used for the design; conventional metals undergo plastic deformation at low strain while elastomer-based designs are often too rigid for the localized deformations needed for high envelopment.
Recent advancements at the NASA Glenn research center in a unique class of metals know as shape memory alloys (SMAs) has opened the design space for non-pneumatic compliant tire technologies allowing designs to incorporate orders of magnitude more deformation without damage. The work presented herein highlights the advantages of using SMAs as compared to conventional metals. Additionally, the development of a unique SMA compliant tire design capable of carrying up to 13.2 kN (3000 lbf) with reversible, local deformations on the order of the side wall height will be presented.

SESSION PM06.09: Other Functional Intermetallics
Session Chairs: Yoshisato Kimura and Matthew Willard
Thursday Afternoon, November 29, 2018
Hynes, Level 1, Room 104

1:30 PM *PM06.09.01
Microstructure and Magnetic Properties of τ – MnAl Ian Baker; Dartmouth College, Hanover, New Hampshire, United States.

τ–MnAl adopts an ordered tetragonal $L1_0$ crystal structure with two atoms per unit cell. It has a theoretical maximum energy product, $(BH)_{max}$, of ~100 kJ/m^3, which is twice that of AlNiCo magnets, and a density-compensated $(BH)_{max}$ that is almost two-thirds the value for SmCo magnets. It has a magnetocrystalline anisotropy constant, K_1, of ~2 MJ/m^3, and thus it is of great interest as a permanent magnet. Fortuitously, it is composed of relatively inexpensive elements. It can be made by heating to above 870ºC to produce the high-temperature hexagonal ε-phase and then either quenching to room temperature and re-annealing at temperatures up to ~500ºC or by simply slow cooling. The transformation introduces anti-phase boundaries, microtwins, stacking faults and dislocations. During the transformation to τ–MnAl it is difficult to avoid some conversion to the equilibrium trigonal $γ_2$ (Al_8Mn_5) and complex cubic β-Mn phases.
In this presentation, we will outline a variety of MnAl processing routes including gas atomization, rapid solidification processing using the Pratt and Whitney RSR process, and casting followed by pulverization to produce MnAl powders. The resulting particulates were mechanically milled to produce nanocrystalline material using a Union Process attritor. The high temperature ε-phase was present both before and after milling along with significant amounts of equilibrium $γ_2$ and β phases. In addition, ribbons were produced by melt spinning, which had a similar mix of ε, β and $γ_2$ phases. We will

outline the effects of annealing on the phases present and the magnetic properties of the various powders and ribbons. We will also present the results of the use of back-pressure assisted equal channel angular extrusion through which the powders are simultaneously consolidated and transformed to the τ phase. The results will be compared with the magnetic properties obtained after various bulk and powder processing techniques.

2:00 PM PM06.09.02
First-Principles Assessment of Nd-Fe-B Thermodynamic Properties for Application in CALPHAD <u>Adie Tri Hanindriyo</u>[1], Soumya Sridar[4], K.C. Hari Kumar[4], Kenta Hongo[3] and Ryo Maezono[2]; [1]Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, Nomi, Japan; [2]School of Information Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; [3]Research Center for Advanced Computing Infrastructure, Japan Advanced Institute of Science and Technology, Nomi, Japan; [4]Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai, India.

The Nd-Fe-B system is of great interest in the field of magnetic materials. Currently commercially available, powerful permanent magnets use the ternary phase $Nd_2Fe_{14}B$ as a base due to its high degree of magnetisation and relatively robust coercivity. The knowledge of phase equilibria and thermochemical properties of Nd-Fe-B system is therefore of great value in the context of optimization of alloy chemistry, manufacturing and application of magnetic materials based on this system.

The CALPHAD method of computational thermodynamics provides a framework to obtain phase equilibria information and thermochemical properties of materials in a cost-effective and efficient manner. The method relies on Gibbs energy functions of constituent phases, which are generated using thermodynamic modeling. Here first-principles calculations of thermodynamic properties can play an important role by means of providing crucial input data required for thermodynamic modeling. These data include formation enthalpy and heat capacity at constant pressure (C_p) for selected phases.

Contribution of localized $3d/4f$ orbitals, which is very important for the system in question, presents a challenge for the *ab initio* framework stemming from exchange-correlation approximation. Mott insulators are also a well-known example of this issue, of the 'strongly correlated' class of materials. To address this challenge, we implement a simplified Hubbard correction under the Density Functional Theory (DFT) framework. We show that this DFT+U method results in relatively reliable values of formation enthalpy, certainly more so than classical exchange-correlation approximation (non-corrected). In order to obtain the phonon frequencies, the forces acting on the atoms in the perturbed supercell are calculated using DFT. C_p is then evaluated under the quasi-harmonic approximation (QHA) to account for volume dependence of phonon frequencies. In contrast to the available data, we find that the computed values deviate considerably from Neumann-Kopp rule. These computational results are expected to improve the reliability of Gibbs energy functions obtained by CALPHAD approach.

2:15 PM PM06.09.03
Influence of Thermo-Mechanical History on Disorder → Order Transformation in 18 Carat Red Gold Alloys <u>Marina Garcia Gonzalez</u>[1,2], Nadine Baluc[3], Steven Van Petegem[1] and Helena Van Swygenhoven-Moens[1,2]; [1]Paul Scherrer Institute, VILLIGEN, Switzerland; [2]IMX - NXMM, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; [3]SPH-ENS, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Residual stress management is a major concern during the processing of 18 carat Au-Cu-Ag red gold alloys. Depending on the thermo-mechanical history and chemical composition of these precious alloys, residual stresses cause reduced workability, shape distortions and eventually fracture. The solid state disorder/order phase transformation forming $Au_{50}Cu_{50}$ nano-precipitates lies at the origin of the problems.

18 carat red gold is an age-hardenable alloy which hardens via chemical ordering. Above the critical temperature (~350°C) the alloy shows a chemically disordered FCC structure. However, below this temperature, chemical ordering takes place and a dispersion of harder nano-precipitates of $Au_{50}Cu_{50}$ phase starts to form. This causes a tetragonal distortion of the initial cubic lattice and induces strong misfit strains. Order/disorder phase transformations are diffusional; therefore, any industrial process that affects the vacancy density and its distribution (such as thermal treatments and plastic deformation) may influence the kinetics of precipitation. This implies that the final microstructure and volume fraction of the ordered precipitates will depend on the history of thermo-mechanical operations.

Our study investigates how thermal parameters and plastic deformation affect the ordering kinetics and the microstructure of the precipitates, with the aim of understanding the link between precipitation and residual stress. *In-situ* x-ray diffraction experiments during cooling are performed at the P07 beam line in PETRA III (DESY, Germany). Diffraction patterns were recorded during cooling, using cooling rates between 100 and 800 K/min. Subsequently, the samples were isothermally aged with and without prior plastic deformation. Rietveld refinement is performed to derive the volume fraction of precipitates. By applying the isothermal JMAEK model, the reaction rates and activation energies are obtained. The results are discussed in terms of the thermo-mechanical history.

2:30 PM PM06.09.04
Microstructure Characterisation of Ni-75 at.% Al Raney Type Alloy as a Result of Cooling Rate and Chromium Doping <u>Naveed Hussain</u> and Andrew M. Mullis; University of Leeds, Leeds, United Kingdom.

The effect of cooling rate on the phase composition of gas atomized Raney type catalysts was studied using the Ni-75 at.% Al composition. The resulting particles were sieved into 3 standard size fractions and analysed using XRD with Rietveld refinement: as expected the three phases, Al_3Ni_2, Al_3Ni, and Al-Al_3Ni eutectic were identified. Differing phase compositions in the 3 size ranges were identified which offer a possible explanation for varying catalytic activity with cooling rate. With increasing particle size, there is more Al_3Ni and less Al_3Ni_2. The amount of Al eutectic also decreases as the particle size increases. This agrees with the expectation that the higher cooling rates experienced by the smaller droplets allow less time for the peritectic conversion of Al_3Ni_2 to Al_3Ni to proceed. This in turn results in a more Al-rich residual liquid, increasing the volume fraction of eutectic. This is further confirmed when analysing the microstructure using SEM backscatter imaging. Al_3Ni_2 was found to be encased in a shell of Al_3Ni characteristic of peritectic reactions. The remainder of the alloy was found to consist of Al-Al_3Ni eutectic. The SEM backscatter imaging also indicated that the larger particles, experiencing slower cooling rate, had a less dendritic and a more globular structure than the smaller particles. Similar Raney type Ni-75 at.% Al doped with 1.5 at.% Cr were synthesised using the same method and sieved into the same 3 standard size fractions. It was found that the Cr doped alloys exhibited a more dendritic character than the undoped samples in the corresponding size fraction, although the material still displayed an increasingly dendritic character with increasing cooling rate. The phase composition found by Rietveld refinement also followed a similar trend to the undoped samples with decreasing amounts of Al_3Ni formed at the higher cooling rates. However, significant amounts of an additional phase, $Al_{13}Cr_2$, were also observed. Rietveld refinement found that a larger amount of $Al_{13}Cr_2$ was present than could be accounted for by the addition of 1.5 at.% Cr . This can be explained by the substitution of Ni onto the Cr lattice, as confirmed by Rietveld refinement. $Al_{13}Cr_2$ was found to be located mostly at the boundary of the Al_3Ni and Al-Al_3Ni eutectic phases during elemental mapping and quantitative image analysis of backscattered electron micrographs. This indicates that precipitation of $Al_{13}Cr_2$ is towards the end of the solidification process. The relatively large amounts of the Al-rich $Al_{13}Cr_2$ may explain the enhanced catalytic activity observed following leaching of Cr-doped Raney catalysts.

2:45 PM PM06.09.05

Nb_3Sn Coatings for Next Generation Particle Accelerators <u>Michael J. Kelley</u>[1], Uttar Pudasaini[1], James Tuggle[2], Grigory Eremeev[3] and Charles Reece[3]; [1]College of William & Mary, Williamsburg, Virginia, United States; [2]Virginia Tech, Blacksburg, Virginia, United States; [3]Thomas Jefferson Laboratory, Newport News, Virginia, United States.

Nb_3Sn has the potential to achieve superior performance in terms of quality factor, accelerating gradient and operating temperature (4.2 K vs 2 K) resulting in significant reduction in both capital and operating costs compared to traditional niobium SRF accelerator cavities. Tin vapor diffusion coating of Nb_3Sn on niobium appears to be a simple, yet most efficient technique so far to fabricate such cavities. Here, cavity interior surface coatings are obtained by a process of nucleation followed by deposition. The first step is normally accomplished with $Sn/SnCl_2$ at a constant low temperature (~500 °C) for several hours. To elucidate the role of this step, we systematically studied the niobium surface nucleated under varying process conditions. The surfaces obtained in typical tin/tin chloride processes were characterized using SEM/EDS, AFM, XPS, SAM and TEM. Examination of the surfaces nucleated under the standard conditions revealed not only tin particles, but also tin film on the surfaces All the nucleation attempted with $SnCl_2$ yielded better uniformity of Nb_3Sn coating compared to coating obtained without nucleation, which often included random patchy regions with irregular grain structure. Even though the variation of nucleation parameters was able to produce different surfaces following nucleation, no evidence was found for any significant impact on the final coating. Coatings cross-sectioned by FIB and examined by EBSD showed columnar structure. Composition measurement by XPS sputter profile showed constant Nb_3Sn composition except adjacent to the interface. Examination of overcoated samples by FIB/EBSD showed growth by formation of new grains at the interface.

3:00 PM BREAK

3:30 PM *PM06.09.06

Phase Evolution of Nanostructured Fe-Si-Al-Based Intermetallic Phases in Soft Magnetic Alloys <u>Matthew A. Willard</u>[1], Maria Daniil[3], Rajesh Jha[2], David Grimmer[2], Aaron Stebner[2] and Cristian Ciobanu[2]; [1]Case Western Reserve University, Cleveland, Ohio, United States; [2]Colorado School of Mines, Golden, Colorado, United States; [3]Bard High School Early College, Cleveland, Ohio, United States.

Nanocrystalline soft magnetic materials are the latest and most promising of the soft magnetic materials that were developed at the end of the 20th century. They have since been studied extensively, and various alloy compositions have been developed and optimized for ambient and extreme (cryogenic and elevated temperature) applications. Their advantage lies in the unique combination of fine microstructure, crystal structure and composition, which can be achieved by rapid solidification and subsequent controlled annealing. In this article, we discuss the requirements and the challenges of the designing these alloys and how it affects the crystal structure, microstructure and eventually the magnetic performance of new alloys designed for use at temperatures below 150K in applications as varied as cryo-power electronics and magnetic shielding. Efforts to use computational materials science to accelerate the alloy design process will be discussed.

4:00 PM PM06.09.07

Composition Dependency of Thermoelectric Properties in Ca-Mg-Si System Using Thin Films Prepared by RF Magnetron Sputtering Method <u>Hiroshi Funakubo</u>[1], Mutsuo Uehara[1], Mao Kurokawa[1], Atsuo Katagiri[1], Kensuke Akiyama[1, 2], Takao Shimizu[1], Masaaki Matsusima[1], Hiroshi Uchida[3] and Yoshisato Kimura[1]; [1]Tokyo Institute of Technology, Yokohama, Japan; [2]Kanagawa Institute of Industrial Science and Technology, Ebina, Japan; [3]Sophia University, Tokyo, Japan.

Ca-Mg-Si ternary system consists of abundant and non-toxic elements. This system includes Mg_2Si that reported to show good thermoelectric properties and realize both p- and n-type conduction. CaMgSi is expected to show good thermoelectric properties. However, the investigation of the thermoelectric property in Ca-Mg-Si system is limited to the narrow composition region. Investigation for wide composition region, possibility of the composition dependency in the sinterability makes a problem to evaluate the thermoelectric property in case of the sintered body. To overcome this problem, we selected thin films that can make dense samples for wide range of composition.
In the present study, films of Ca-Mg-Si system were prepared by RF magnetron sputtering system and thermoelectric properties were investigated for wide composition region. Films with wide composition range were successfully obtained on $(001)Al_2O_3$ substrates at the deposition temperature of 260-340 °C using Mg target with various numbers of Ca and Si chips. Obtained films were post heat treated at 500–700 °C under the 5% H_2 included Ar atmosphere. Conduction type of the films mainly changed by the $Si/(Ca+Mg+Si)$ ratio of the films and p-type and n-type conductions were observed below 0.6 and above 0.7, respectively. Single phases of CaMgSi and $Ca_7Mg_{7.25}Si_{14}$ were successfully obtained and showed p-type. Maximum power factor of 0.15 $mW/(mK^2)$ at 400 °C was obtained for the films with Ca:Mg:Si = 0.2:0.2:0.6. In our presentation, we show the systematic data of the crystal structure and thermoelectric properties as a function of film composition.

4:15 PM PM06.09.08

Enhancing Thermoelectric Properties through Control of Nickel Interstitials and Phase Separation in Heusler/Half-Heusler $TiNi_{1.1}Sn$ Composites <u>Emily E. Levin</u>, Francesca Long, Jason Douglas, Malinda Buffon, Leo Lamontagne, Tresa Pollock and Ram Seshadri; University of California, Santa Barbara, Santa Barbara, California, United States.

Heusler intermetallics, including compounds crystallizing in the F–$43m$ half-Heusler and Fm–$3m$ full-Heusler crystal structures, are known for their diverse functional properties, a consequence of their wide chemical tunability. At intermediate compositions between the half-Heusler and full-Heusler, some systems appear to phase separate while others form complete solid solutions. This differing behavior constitutes an additional tuning parameter in the development of these compounds as functional materials. Here we discuss the half-Heusler/Heusler system $TiNi_{1+x}Sn$ ($0 \leq x \leq 1$) where a driving force for phase separation exists. However, we have found that appropriate heat treatment can trap Ni interstitials by design, in order to strongly accentuate the thermoelectric properties.[1] Rietveld analysis of synchrotron X-ray diffraction confirms the incorporation of Ni interstitials into the half-Heusler, and electron microscopy illustrates the evolution of microstructure with heat treatments. Half-Heusler samples with Ni interstitials display an enhanced Seebeck coefficient due potentially to in-gap states and modification of the carrier concentration,[2] leading to an improved power factor. Furthermore, Ni interstitials act as point defects, scattering phonons and reducing thermal conductivity, leading to over fivefold increase in room temperature figure of merit compared to homogenized $TiNi_{1.1}Sn$. Further annealing at low temperature allows the excess Ni to diffuse, forming full-Heusler nanoprecipitates which also act to scatter phonons and lead to over 2× increase in the figure of merit as compared to homogenized $TiNi_{1.1}Sn$.

[1] E. E. Levin, F. Long, J. E. Douglas, M. L. C. Buffon, L. K. Lamontagne, T. M. Pollock and R. Seshadri, Enhancing thermoelectric properties through control of nickel interstitials and phase separation in Heusler/half-Heusler $TiNi_{1.1}Sn$ composites, *Materials* **11** (2018) 903.
[2] K. Miyamoto, A. Kimura, S. Sakamoto, M. Ye, Y. Cui, K. Shimada, H. Namatame, M. Taniguchi, S. Fujimori, Y. Saitoh, E. Ikenaga, K. Kobayashi, J. Tadano, and T. Kanomata, In-gap electronic states responsible for the excellent thermoelectric properties of Ni-based half-Heusler alloys, *Appl. Phys. Exp.* **1** (2008) 081901.

4:30 PM PM06.09.09

Kinetic Analysis of Crystallization Reaction Within Co-Sn Alloy <u>Muna S. Khushaim</u>[1,2], Fatimah Alahmary[2], Ahmad Al-Joraid[1] and Torben Boll[3]; [1]Taibahu University, Almedinah, Saudi Arabia; [2]King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; [3]Karlsruhe Institute of Technology–Institute for Applied Materials, Karlsruhe, Germany.

Co-Sn alloy is an important system for Sn- based anode materials of lithium ions batteries due to the different interesting intermetallic compounds nucleate and grow during crystallization reaction. These compounds are: $CoSn$, $CoSn_2$ and $CoSn_3$. These intermetallic compounds, which are containing Sn, are important as anode materials in order to provide a means for efficient Li storage. Co–Sn alloys are applied in specific high-tech applications; and hence study the kinetics of the crystallization reaction of this system and the dependency of the activation energy for crystallization of different intermetallic phases on the temperature might provide a method to control the reaction and the synthesized products. Moreover, a critical knowledge about the growth mechanism will assist in the understanding of the of the melting – solidification region within Co-Sn system. In this study, Co: Sn alloy with ratio of approximately 1:3 were prepared by using metal flux method using arc-melter technique. Microstructure characterizations of the samples have been done by using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The alloy was heated under a non-isothermal condition by using differential scanning calorimetry (DSC) at different heating rates. After observing the exothermic changes which indicate to the crystallization of different intermetallic phases during the DCS scanning, different isoconversional methods were applied in order to determine the variation of the activation energy of crystallization with temperature. In order to shed light on a segregation of atoms at the interface between the metal flux and different intermetallic phases, and hence understanding the growth mechanism of the observed intermetallic phases, atom probe tomography (APT) is used. Using APT as a sophisticated tool allowed us to obtain a critical knowledge of nano scale evolution of the microstructure and investigate the intermediate steps in the mechanism of flux-grown intermetallic phases. The results obtain from APT analysis in combination with the calculation of the variation of activation energies of different intermetallic phases with the temperature provide new combined methods to investigate the kinetic of crystallization reaction within Co-Sn alloy.

4:45 PM PM06.09.10

Room Temperature High Pressure Hydrogen Storage in Mg_2Ni Nnanoparticles Decorated Frustule-Nitrogen Doped Graphene S. Ramaprabhu and <u>Sai Smruti Samantaray</u>; Indian Institute of Technology Madras, Chennai, India.

Hydrogen as an alternative energy carrier is a promising solution for reducing CO_2 emissions and its related adverse effects on the environment. However, lack of an economically viable, safe and efficient storage method is a significant barrier between its production and use. This problem arises mainly due to the low energy per unit volume of hydrogen under ambient conditions. Hydrogen storage in metal hydrides is a better option in comparison to the conventional hydrogen storage methods in terms of safety, but the requirement of high temperatures for the dissolution of the adsorbed hydrogen is disadvantageous. Magnesium based materials have the potential as good hydrogen storage materials and have been widely investigated. But, their practical utilization is hindered by poor thermodynamics and sluggish dehydrogenation kinetics. With the aim of overcoming this barrier, we have synthesized low cost Mg based alloy nanoparticles decorated frustule –nitrogen doped graphene (Mg_2Ni-N-D-G) and investigated its hydrogen storage properties. The underlying hydrogen storage mechanism in the synthesized nanocomposite is the spillover effect. Mg_2Ni decorated nitrogen doped graphene (Mg_2Ni-N-G) systems have been previously studied in our laboratory and a hydrogen storage capacity of ~4 wt% at room temperature and moderate hydrogen equilibrium pressures has been obtained. Combining this with the unique physical and chemical properties of diatom frustules such as large surface area, chemical inertness and good porosity has proved to be fruitful for hydrogen storage. Hence, the synthesized nanocomposite Mg_2Ni-N-D-G is explored as a potential hydrogen storage material to obtain a gravimetric density of ~ 5wt% at room temperature and moderate hydrogen pressure.