

ABSTRACTS

Monday 10:45

Precipitation Behavior of C14 Laves Phase $(\text{Fe,Cr})_2(\text{Nb,Mo})$ in αFe -based Alloys with High Cr Content

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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 homogeneous distribution of C14 Laves phase, while gradient distribution with large volume fraction would be desirable for functional applications mentioned above. The objectives of the present work are to understand the precipitation behavior of C14 Laves phase $(\text{Fe,Cr})_2(\text{Nb,Mo})$ in Fe-20Cr-0.5Nb-xMo-ySi (x=0–2, y=0–2) quaternary αFe -base model alloys, and to determine the growth mechanism of C14 Laves phase in the bcc αFe matrix.

The precipitation behavior of C14 Laves phase in the αFe matrix was characterized for Fe-20Cr-0.5Nb-xMo (x=0–2) alloys annealed at 1073 K for 0.5–168 hours after cold rolling of the 70% reduction rate in thickness. C14 Laves phase starts to precipitate within 0.5 hour not only preferably on grain boundaries but also interior of αFe grains. The growing stage continues longer than 24 hours before the coarsening stage, according to microstructure observation and chemical composition measurements for solute concentration in the αFe matrix. The growing mechanism of C14 Laves phase was determined to be the ledge mechanism on the $(-110)_{\alpha} // (0001)_{\text{C14}}$ habit planes as terrace planes in an Fe-20Cr-0.5Nb-2Mo alloy 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 plate shape depending on the anisotropic difference of lattice mismatch.

The addition of Si together with Mo remarkably enhances the precipitation of C14 Laves phase. For instance, the area fraction of C14 Laves phase increases about twice as large in an Fe-20Cr-0.5Nb-2Mo alloy 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, Si is not effective to increase C14 Laves phase precipitation on a Mo-free Fe-20Cr-0.5Nb alloy. It is suggested that 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. The lattice mismatch between the bcc αFe and C14 Laves phase decreases as the Mo content increases, which might lead to the uniform distribution of C14 Laves phase precipitation particles.

Monday 11:10

"Reactive" Microstructure of High Performance Ferritic (HiperFer) Steels, the Key to Fatigue-resistant High-temperature Materials

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Future, flexible thermal energy conversion systems require new, demand-optimized high-performance steels. In order to provide a basis for the targeted development of fatigue-resistant, cost-effective steel grades, the microstructural damage to materials and the failure of conventional ferritic-martensitic 9-12 Cr steels in thermomechanical fatigue tests were investigated. Based on the findings, improved ferritic "HiperFer" (High performance Ferritic) steels were designed, manufactured and characterized. These steels are strengthened by $(\text{Fe,Si,Cr})_2(\text{Nb,W})$ - Laves phase precipitates and feature strongly improved steam oxidation, downtime corrosion, creep and fatigue strength properties. The microstructural mechanism of strengthening against fatigue will be addressed and the current state of alloy development will be described.

Monday 11:35

Thermomechanically Induced Laves Phase Precipitation in High Chromium Ferritic Stainless Steels

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Fully ferritic, Laves phase strengthened, stainless steels with a chromium content of 17 wt.-% show potentially sufficient resistance to steam oxidation at high temperatures. This class of steel is designed to be used in the next generation of super critical thermal power conversion systems. Creep strength cannot be achieved based on the precipitation of carbides, nitrides and carbonitrides in this alloying system, because of the low solubility of carbon and nitrogen in ferritic steel. Alloying by tungsten, niobium and silicon enables the desired combination of outstanding oxidation resistance and creep strength by solid solution and precipitation strengthening effects by finely dispersed intermetallic $(\text{Fe,Si,Cr})_2(\text{Nb,W})$ - Laves phase particles. The main design tasks were minimization of the unwelcome, potentially embrittling (Fe,Cr) σ -phase and maximization of the amount of strengthening Laves phase particles.

The presented research focusses on so called “integrated processing” and aims towards fundamental understanding of the interaction of alloy composition, thermal/thermomechanical treatment during production (i.e. soaking, forging, rolling, interpass annealing, recrystallization) and the resulting microstructure and mechanical properties.

Monday 12:00

Thermokinetic Simulation of Laves Phases Precipitation in High Cr Steels

Aurélié Jacob, Erwin Povoden-Karadeniz

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Development of new materials with specific application can be shortened by using computational tools to predict the behaviour of the material during operating conditions. Prediction of the microstructure evolution is based on thermodynamic and kinetic databases developed for multicomponent systems.

In the development of high Cr ferritic steels strengthened by Laves phase particles [1,2], it was shown that there is a lack of describing the stability of Laves phase [3,4] by using commercial thermodynamic databases (i.e. TCFe). These databases are based on the thermodynamic optimization of sub-ternary and binary systems. A comprehensive literature survey has shown that many of the sub-systems containing Laves phase were not properly described.

In the present work, we have developed a thermodynamic database including the description of Laves phase taking into account the change of polytype (C14 and C15) as well as the dissolution of Si which is promoting and stabilizing the Laves phase.

Revised thermodynamic modeling of Laves phase containing systems [5–8], based on experiments [7,9,10] were added to multicomponent thermodynamic database and used to calculate the formation and stability of Laves phases in high Cr ferritic steels. The thermodynamic database was then used for the thermokinetic simulation of precipitation of Laves phase in steels, taking into account different nucleation sites, including dislocations and grain boundaries. Results are discussed in the framework of optimised alloy and process design for improved mechanical product properties.

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Monday 13:30

Design of Heat Resistant Ferritic Steels Using Laves Phase Precipitation

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Heat resistant ferritic (martensitic) steels are widely used for high temperature components such as main steam pipes and turbine rotors in fossil fired power plants due to their relatively low costs, high strength and low thermal expansion coefficients. Carbonitride and carbide phases are generally considered to strengthen and stabilize the transformed ferritic matrix. These secondary phases are, however, coarsened and/or decomposed after long-term creep deformation and thereby losing their strengthening effects and limiting the life of currently available ferritic steels.

Laves phases, such as Fe_2Mo and Fe_2W , are known to be precipitated during creep deformation in conventional heat resistant ferritic steels. They appear as fine plate-like particles or as coarse globular grains at the lath/block/packet boundaries. We recently found the formation of periodically arrayed rows of very fine Fe_2Hf Laves phase particles in massively transformed 9% Cr ferritic matrix. Our studies have revealed that the fine Fe_2Hf phase is formed through interphase precipitation along the eutectoid type pathway of δ -ferrite \rightarrow γ -austenite + Fe_2Hf and a subsequent phase transformation from γ to α -ferrite. The effects of Laves phase type on the creep resistance and the microstructural stability have not, however, been fully understood.

In the presentation we will show microstructural features and formation kinetics of the fine Fe_2Hf Laves phase particles in 9% Cr based ferritic steels, creep properties of the fine Laves phase strengthened ferritic steels and the coarsening behavior of different Laves phase types. Based on available knowledge we will propose a new alloy design concept using Laves phase to improve long term creep resistance of ferritic steels.

Monday 13:55

Effects of Hf and Cr Contents on the Formation of Fe₂Hf Laves Phase through Interphase Precipitation in Fe-Cr-Hf Ternary Alloys

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In conventional ferritic heat resistant steels, M₂₃C₆ carbide or MX carbonitride precipitates are used to strengthen the martensitically transformed matrix. Coarsening and/or decomposition of the precipitates, however, occurs during creep, which results in a degradation of the strength of the materials. The Laves phase is promising as a strengthening phase in ferritic heat resistant steels due to relatively high thermodynamic stability at high temperatures. A fine dispersion of Fe₂Hf-Laves phase formed through an interphase precipitation is of interest as a new strengthening way although the heat treatability is poor; the interphase precipitation (δ -Fe \rightarrow γ -Fe+Fe₂Hf) is competitive with the precipitation of Laves phase from the δ phase in the eutectoid-type reaction pathway ($\delta \rightarrow \delta$ +Fe₂Hf). In the present paper, the effect of supersaturation on the precipitation of Laves phase from δ phase ($\delta \rightarrow \delta$ +Fe₂Hf) and the $\delta \rightarrow \gamma$ transformation in the reaction pathway by changing the Hf and Cr contents.

Time-Temperature-Transformation (TTT) diagrams were constructed in a series of ternary alloys; the Hf content was changed from 0.06~0.12 at.% while the Cr content was fixed as ~9.5 at.% in Series I; the Hf content was fixed at 0.1 at.% while the Cr content was changed from 8.5~10.5 at.% in Series II. The increase in Hf content (Series I) widened the temperature range for interphase precipitation toward higher temperature but retarded the onset of $\delta \rightarrow \gamma$ transformation and thereby promoting the $\delta \rightarrow \delta$ +Fe₂Hf reaction. A reduction of Cr content (Series II) promoted the $\delta \rightarrow \gamma$ transformation and thereby suppressing the $\delta \rightarrow \delta$ +Fe₂Hf but too much reduction also suppressed the interphase precipitation probably because the rate of the δ/γ interface migration is too rapid for precipitation. The results obtained suggest that it is effective to have a high supersaturation for the precipitation of Laves phase and an adequately high supersaturation for the $\delta \rightarrow \gamma$ transformation at the same time in order to widen the window of the interphase precipitation.

Monday 14:20

Strengthening of Iron Aluminide Alloys by Laves Phases

Martin Palm

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Lack of strength at high temperatures inhibited any wider application of iron aluminide alloys for long times. However, new alloy concepts led to materials with sufficient strength at least up to 750 °C. One of these new concepts is the strengthening by precipitates of Laves phases.

Though the idea of strengthening iron aluminides by precipitates of another intermetallic phase is not new, the even and fine distribution of these phases within the microstructure poses a problem. However, in Fe-Al-Ta alloys nanometer-sized precipitates of coherent Heusler phase (Fe_2TaAl ; L_{21}) form within the Fe-Al matrix, which lead to considerable strengthening of the alloys. But it has been shown that the Heusler phase is actually a metastable phase. Above 750 °C or after annealing below 750 °C a Laves phase ($(\text{Fe,Al})_2\text{Ta}$; C_{14}) forms instead.

The formation of metastable Heusler phase and Laves phase have now been studied in more detail. Based on these results, measures have been established to control the precipitation of the Laves phase. Through heat treatments, doping or pre-deformation, different types of distributions of the Laves phase within the microstructure can be obtained. Preliminary creep tests at 700 °C show that if the Laves phase is precipitated along grain boundaries, the strength of the alloy matches that of an alloy with coherent Heusler precipitates. The results also show that besides precipitation hardening, solid solution hardening markedly contributes to the strength of the alloys. *Post mortem* examination of the crept samples revealed no crack formation around the Laves phase at the grain boundaries.

Monday 14:45

Laves Phase in Alloy Systems including Nb, Al and Si

Seiji Miura ¹, Li Peng ², Toshiaki Horiuchi ³, Ken-Ichi Ikeda ¹, Satoshi Takizawa ¹

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For designing refractory-metal based high temperature alloys, B2 aluminide coating is one of the solutions for improving oxidation resistance. However, it is pointed out that brittle ternary Laves phase such as Nb(Ni,Al)₂ with MgZn₂-structure (C14) appears in Nb-Ni-Al ternary phase diagram between bcc-Nb and B2-NiAl, which may cause cracking. On the other hand, the introduction of Laves phase as precipitates might be another choice for strengthening. Authors have conducted experimental investigations on the microstructure evolution in Cr-Mo-Nb system and the phase stability in Nb-Mo-Ni-Al-Si system.

In the isothermal sections of the Cr-Mo-Nb ternary system, there is a three-phase region composed of Cr-rich BCC1, Cr-lean BCC2 and C15 NbCr₂ Laves. In the Cr-rich side, the Laves phase appears grain interior homogeneously with a certain crystallographic orientation relationship with Cr-rich BCC matrix. On the other hand, in Cr-lean side, the Laves phase appears mainly at BCC-BCC grain boundary, and no crystallographic orientation relationship was found. The difference of precipitation behavior is discussed in terms of the lattice mismatch. In three-phase region, after the decomposition of BCC phase into BCC1 and BCC2, the Laves phase appears at around Cr-rich BCC1 phase. It is due to lower lattice mismatch with Cr-rich BCC1 than that with Cr-lean BCC2. NbCr₂ Laves phase shows high nano-hardness of about 14.5 GPa, which causes high strength of alloys. However, in the alloy with three-phase microstructure, the size of Laves phase was kept to be a few micrometers and there were almost no crack from the corner of Vickers indents [1].

In the Cr-Mo-Nb phase diagram, it was found that Mo tends to occupy Nb site in NbCr₂ Laves phase, while there is no MoCr₂ Laves phase [1]. The stability of binary Laves phase is strongly affected by the size of constituent elements. In Nb-Ni-Al ternary system, authors have found that the average size of NiAl estimated from the lattice constant of B2 phase is important to understand the stability of Nb(Ni, Al)₂ Laves phases [2]. From this point of view, it is expected that the addition of smaller Si stabilizes the ternary Laves phases composed of Nb, Al and transition elements. A systematic investigation for understanding the Laves phase in Nb-Mo-Ni-Al-Si system is performed. The results strongly suggest a wide continuous solid solution of Laves phase among Nb(Ni,Al)₂, Mo(Ni,Si)₂ and off-stoichiometric Nb(Ni,Si)₂. We have also performed ab initio calculations based on the density functional theory and obtained formation energies for the C14-type structures to examine the above experimental results. The package produced by the abinit project [3] was employed for the numerical computations. The results show that the Nb(Ni,Al)₂ and Mo(Ni,Si)₂ Laves phases are stable while the Mo(Ni,Al)₂ Laves phase is unstable. This result is in good agreement with the experimental results.

This work was supported by a grant from the Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST) (No. JPMJAL1407). A part of this work was conducted at the Laboratory of Nano-Micro Materials Analysis, Hokkaido University, supported by the “Nanotechnology Platform” Program of MEXT, Japan.

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Monday 15:40

Origin and Progress of the Austenitic Laves Steels

- Design Approaches and Strengthening Mechanisms -

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About 20 years ago, several questions were raised up in my mind: how high the temperature capability of the austenitic heat-resistant steels can be increased; why there are no austenitic heat-resistant steels strengthened by intermetallic phases; is it really true that topologically close-packed (TCP) phases are detrimental? In conventional austenitic heat-resistant steels, TCP phases consisting of transition metal (M) elements, such as Laves ($C14$, $hP12$) and Sigma ($D8_b$, $tP30$) phases, are commonly observed at their grain boundaries (GBs) after prolonged aging at elevated temperatures. Thus, it has been believed blindly that the formation of TCP phases give rise to the degradation of creep properties in these steels. In addition, because of their brittle nature associated with their complicated crystal structures, they are regarded as harmful phases. If this thought is correct, however, how about transition metal carbides, such as $M_{23}C_6$ ($D8_4$, $cF116$) and MC ($B1$, $cF8$)? Do they deform? These carbides are even harder than TCP phases and commonly used as strengthening species in the heat-resistant steels. My conclusion was that, it is not the TCP phase but the microstructure instability of the carbides changing to TCP phases that causes the degradation. In order to verify the thought, carbon free model steels strengthened by the TCP phases have to be designed. This is the trigger of the R & D of the novel austenitic heat-resistant steels strengthened by Laves phase, called “**Austenitic Laves Steels (ALS)**”. Then, we originally proposed the design concept of the ALS, and subsequently the idea has been taken and coming down to ORNL, Tsinghua University and Dartmouth College groups.

In this talk, the design approaches and recent advances of ALS are presented. The design principle of ALS is in phase diagram study of Fe-Ni-M ternary systems, and the knowledge is extended to Fe-Ni-Cr-M multi-component systems. A newly designed ALS exhibits superior creep properties at 1073 K to those of any other steels and almost equivalent to Ni-based alloys. The superior creep strength is caused by precipitation of Fe_2Nb Laves phase at GBs. The higher the fraction of grain-boundaries covered by the Laves phase (p), the lower the creep rate ($\dot{\epsilon}$), with following relationship: $\dot{\epsilon} = \dot{\epsilon}_0(1-p)$. This strengthening method, named “**Grain-boundary precipitation strengthening (GBOS)**”, is effective at $p > 80\%$ under low stress levels. The design principle can be applied to other TCP phases in Ni base alloys.

Part of this study was carried under the research activities of “Advanced Low Carbon Technology Research and Development Program” (ALCA) in JST (Japan Science and Technology Agency).

Monday 16:05

Deformation Mechanisms of the Laves Phases in the Mg-Al-Ca System

Christoffer Zehnder, Konrad Czerwinski, Stefanie Sandlöbes, James S. K.-L. Gibson, Sandra Korte-Kerzel (presenting author)

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In order to improve the creep resistance of magnesium alloys and thereby increase their operating temperature, hard intermetallic phases can be incorporated in the microstructure. In particular the addition of Al or Ca to Mg results in the formation of a skeleton-like intermetallic structure. This structure consists predominately of Laves phases, which reduces the minimum creep rate by a few orders of magnitude. In bulk, these Laves phases are extremely brittle at low temperatures, limiting our understanding of the underlying mechanisms of plasticity. Additionally, the small size of the microstructural features in technical alloys make bulk-scale tests unsuitable for studying these phases. Using nanomechanical testing (nanoindentation and microcompression) in individual grains, cracking can be suppressed and plastic deformation can be observed [1]. Micropillars were milled using FIB in individual grains of a polycrystalline specimen, and orientations determined by EBSD to activate and interrogate slip systems. These data have then been combined with slip line analysis around indents. Such an approach reveals the presence of pyramidal, prismatic and basal slip at ambient conditions, with pyramidal 1st order being the predominant slip plane. Critical resolved shear stresses for these slip systems have been calculated, and TEM analysis of the deformation microstructure performed. DFT was used to simulate the syncroshear mechanism in the basal plane displaying a first step towards simulating the other slip planes. This work therefore exemplifies how nanomechanical testing in conjunction with electron microscopy can extend the current knowledge of plasticity in macroscopically brittle crystals.

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Monday 16:30

Composition Dependence of Mechanical Properties of the Cubic and Hexagonal NbCo₂ Laves Phases Studied by Micromechanical Testing

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Laves phases are the largest class of intermetallic phases and they are promising candidates for high-temperature applications due to their high melting point, high strength and good creep resistance. However, the knowledge of their mechanical properties is still limited and the effect of the composition, crystal structure and orientation on their mechanical properties is not well understood yet. A well-suited system to study these effects in Laves phases is the Co-Nb system. Here, the NbCo₂ Laves phase exists over an extended composition range from approximately 24 to 37 at.% Nb and the stable crystal structure type changes from the hexagonal C36 variant via cubic C15 to hexagonal C14 with increasing Nb content allowing a simultaneous study of the dependence of mechanical properties on composition and crystal structure.

The pronounced brittleness of Laves phases makes the preparation and mechanical testing of bulk Laves phase alloys challenging and time-consuming. In order to circumvent the difficulty of preparing and testing bulk Laves phase alloys and to study the effect of composition on the mechanical properties of the cubic and hexagonal NbCo₂ Laves phases in detail, a new method, which is to combine the diffusion couple technique and micromechanical testing, is used in the present work. By using the diffusion couple technique, thick diffusion layers of the C36, C15 and C14 NbCo₂ Laves phases with concentration gradients covering the complete homogeneity ranges of these phases were grown. The defects at different positions on the surface of the diffusion couples were observed by the ECCI technique. The defect state as a function of composition was analyzed. Single-phase and single crystalline micropillars of NbCo₂ with different compositions were cut in the diffusion layers by the FIB milling technique and their critical resolved shear stress (CRSS) was measured by *in-situ* micropillar compression tests. The hardness and Young's modulus of NbCo₂ as a function of composition at room temperature were probed on the diffusion couples by nanoindentation. The composition dependence of mechanical properties including hardness, Young's modulus and CRSS of the cubic and hexagonal NbCo₂ Laves phase will be shown and discussed in the presentation.

Monday 16:55 (Poster)

Poster 1:

Laves Phases in Industrial Zirconium Alloys

Caroline Toffolon-Masclet¹, Joel Ribis¹, Jean-Christophe Brachet¹, Paul Lafaye², Jean-Claude Crivello³ and Jean-Marc Joubert³

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Zirconium alloys are currently used as fuel cladding materials in Pressurized Water Reactors (PWR). In-service conditions, these alloys are subjected to multiple constraints: very corrosive and radiative environment, mechanical stresses. Furthermore, in hypothetical accidental conditions, they would be submitted to high temperature transients leading to an increase of oxidation and mechanical stresses.

These alloys are multi-alloyed materials. Thus, in this study we will focus on two industrial alloys: low tin Zircaloy-4 (Zr-1.3wt%Sn-0.2wt%Fe-0.1wt%Cr-0.13wt%O) and Zr-1Nb(O) (Zr-1wt%Nb-0.03wt%Fe-0.13wt%O). The presence of Fe, Cr and/or Nb may induce the precipitation of different Laves Secondary Precipitated Phases (SPPs).

More recently, new Zr alloys are being developed in the framework of improvement of the LWR reactors safety, and more specifically the accident tolerance of the nuclear fuel subassembly. One way to do that is to develop Zr claddings with high adherent protective Cr-coating in order, in particular, to reduce the high temperature oxidation rate of these alloys. Development of such alloys requires multi-scale characterizations: hence, depending on the Cr coating deposition process and the material substrate, Zr/Cr precipitation of $Zr(Fe,Cr)_2$ nanolayers with both C14 and C15 structures have been sometimes observed at the chromium-zirconium interface [1]. Then, a good knowledge of these interfacial intermetallic phases and their stability upon in-service or hypothetical conditions is of great importance because they may strongly influence the bonding strength of the chromium coating (coating spallation has to be avoided).

Overall, a good knowledge of the microstructure and especially of the potential occurrence of SPPs in these alloys is thus of high importance considering the influence of microstructure on mechanical properties and corrosion resistance. We are currently developing tools aiming at predicting those microstructures and one of them is a thermodynamic database for zirconium alloys. It allows a better understanding of phase transformations as a function of temperature and chemical composition variations, but also to forecast the precipitation of phases as a function of alloying element variations. Recently, this database has been improved by including systematic DFT calculations of formation enthalpy of intermetallic phases, and in particular of all the Laves phases present in the different system [2].

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[2] P. Lafaye, PhD-thesis (2017)

Monday 16:55 (Poster)

Poster 2:

Structural Diversity of Laves Phases

Fabian Eustermann, Stefan Seidel, Christopher Benndorf, Frank Stegemann, Oliver Janka, Rainer Pöttgen

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In the series RE_2TAl_3 ($RE = Sc, Y, La-Nd, Sm, Gd-Lu$; $T = Ru, Rh, Ir$) several rare earth metal containing pseudo ternary compounds could be characterized. For RE_2RhAl_3 ($RE = La-Nd$) the cubic $MgCu_2$ type is found, while the smaller lanthanides crystallize in the hexagonal Laves phase ($MnZn_2$ type) as well as the complete ruthenium and iridium series. Single crystal data and physical properties were collected from various samples of the three series.^[1]

The ternary gallide $Yb_6Ir_5Ga_7$ ^[2] is the first ordered representative of the so-called $A'(NbIrAl)$ phase, $Nb_{35.50}Ir_{22.22}Al_{42.28}$.^[3] Meanwhile single crystal and powder diffraction measurements revealed that the $RE_6Ir_5Ga_7$ ($RE = Sc, Y, Nd, Sm, Gd-Lu$) gallides are isotypic.^[4] The structure could be described as lonsdaleite-like network of the lanthanide atoms. In the cavities of these network two different rods of condensed Ir_3Ga and $IrGa_3$ tetrahedra are orientated along the hexagonal axis.

With the RE_2Rh_3Ga series ($RE = Y, La-Nd, Sm, Gd-Er$) another example of an ordered Laves-type phase could be determined via single crystal measurements. The samples crystallizes in the rhombohedral Mg_2Ni_3Si type, space group $R\bar{3}m$. The magnetic properties could be determined for all synthesized samples. For Ce_2Rh_3Ga the measurements revealed an intermediate cerium valence. For the diamagnetic representative Y_2Rh_3Ga the ^{89}Y and ^{71}Ga solid state nuclear magnetic resonance spectra shown, as expected for an ordered bulk phase, a single resonance.^[5]

In the 1970's and 1980's Parthé and coworkers published a concept to describe complex structures as intergrowth of the binary Laves phases and $CaCu_5$ related structures. In these publications, the series $RE_{2+n}T_{3+3n}X_{1+2n}$ is mentioned,^[6, 7] which could be used to describe the following example of complex Laves-based structures. A single crystal of YRh_2Ga revealed a new intergrowth variant of $MgNi_2$ and $CeCo_3B_2$.^[8] This new gallide is the $n = 1$ member of the $RE_{2+n}T_{3+3n}X_{1+2n}$ structure series^[6, 7] and crystallizes in the space group $P6_3/mmc$ with the Wyckoff sequence k^2f^3edcba (Pearson code $hP48$). The structure could be described as a $MgNi_2$ tetrahedral network sliced at the mirror planes at $z = 1/4$ and $z = 3/4$ and three inserted additional layers of ordered $CaCu_5$ related slabs ($CeCo_3B_2$ -type). Through these interlayers the three-dimensional tetrahedral network of the $MgNi_2$ structure part decrease to a two-dimensional one.^[8]

Another example for intergrowth compounds are the ternary gallides $RE_4Rh_9Ga_5$, $RE_5Rh_{12}Ga_7$ and $RE_7Rh_{18}Ga_{11}$ ($RE = Y, La-Nd, Sm, Gd, Tb$).^[9] All fourteen synthesized samples could be described as the $n = 2, 3$ or 5 members of the $RE_{2+n}T_{3+3n}X_{1+2n}$ structure series.^[6, 7] In this case the Laves phase part could be described by the cubic one ($MgCu_2$ type) with Mg_2Ni_3Si as

ternary variant. For all samples structure refinements led to $R\bar{3}m$ as correct space group. The structure could be described as MgCu_2 slabs separated by a different number (n) of CaCu_5 related slabs. From the three gallides $\text{RE}_4\text{Rh}_9\text{Ga}_5$ ($\text{RE} = \text{Y, Gd, Tb}$) the temperature dependence of the magnetic susceptibility could be determined in the temperature range of 3–300 K. The yttrium sample shows Pauli paramagnetic behaviour, while the gadolinium and terbium ones exhibit signs of ferromagnetic ordering below the Curie temperature.^[9]

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Monday 16:55 (Poster)

Poster 3:

Experimental Investigation and Thermodynamic Re-assessment of the Fe-Zr System

Ivan Saenko^{1,2}, Boburjon O. Mukhamedov³, Alena V. Ponomareva³, Mario J. Kriegel¹, Alexander L. Udovsky^{2,4}, Olga Fabrichnaya¹, Igor A. Abrikosov^{3,5}

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Composite materials based on high-alloyed steels reinforced by zirconia ceramics are of particular interest due to the wide range of their possible technological applications especially in automotive production. An example of these composite materials is the high-alloyed austenitic stainless TRIP-steel (Transformation Induced Plasticity) reinforced by MgO-stabilized zirconia (Mg-PSZ). The TRIP-Matrix-Composite material exhibits excellent mechanical properties such as high strength values, plasticity, ductility and extraordinary high values of specific energy absorption [1]. The ceramic particles of Mg-PSZ as well as the steel matrix undergo a martensitic transformation during deformation that results in additional strength increase [2].

Development of such composite materials requires the knowledge of thermodynamic properties and phase relations. Therefore, the aims of the present work are the experimental and theoretical study of the thermodynamic properties of the Zr_3Fe and $ZrFe_2$ compounds and thermodynamic re-assessment based on current results. Obtained thermodynamic description will be used for thermodynamic modeling of a multi-component system allowing calculation of the interfacial reactions between TRIP steel and reinforcing ceramic particles.

Theoretical calculations of thermodynamic properties for the Zr_3Fe and $ZrFe_2$ compounds have been performed in the frames of density functional theory (DFT) using Vienna Ab-initio Simulation Package. Effect of finite-temperatures was taken into account within the frames of quasi-harmonic approximation. The thermal expansion coefficient, the bulk modulus, as well as enthalpy of formation, standard entropy as well as heat capacity at constant volume (CV) and at constant pressure (CP) have been calculated for both compounds from 0 K up to high temperatures.

Experimentally, samples of the Zr_3Fe and $ZrFe_2$ compounds have been prepared using Arc-melting method in the Ar-atmosphere. Their chemical compositions were chosen according to their stoichiometric composition. The phase assemblages of the samples have been examined using the X-ray powder diffraction (XRD) and scanning electron microscopy combined with dispersive X-ray spectrometry (SEM/EDX). The heat capacities of both compounds have been measured using differential scanning calorimetry (DSC) method. Heat capacity of the Zr_3Fe compound was measured for the first time in the temperature range between 100 K and 1023 K. Experimental data on the heat capacity of the $ZrFe_2$ have been

obtained in the wide temperature range from 100 K to 1473 K and compared with available literature data. Based on the combination of theoretical and experimental data, the main thermodynamic properties of the Zr_3Fe and ZrFe_2 compounds were described from 0 K up to temperatures close to the limits of their stability.

Based on the obtained experimental and DFT data, using available phase equilibrium [3] and calorimetric data [4] thermodynamic parameters of the Zr–Fe system were re-assessed.

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Monday 16:55 (Poster)

Poster 4:

Phase Relations in the Co-rich Part of the Co-Ti System including the Coexisting C36 and C15 Laves Phases

Maisam Merali^{1,2}, Frank Stein¹

¹ Department of Structure and Nano-/Micromechanics of Materials, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany; ² student at St. Catherine's College, University of Cambridge, Cambridge, UK

The Co-Ti system is one of the important systems for the development of Co-based superalloys and the only binary Co-X system forming coherent γ/γ' microstructures (fcc-Co with fcc TiCo₃). Surprisingly, the phase relations and invariant reaction temperatures in the Co-rich part of the system are not very well established. Especially interesting is the occurrence of two polytypes C15 and C36 of the Laves phase TiCo₂. Contradicting information exists about the existence and width of a two-phase field between the two Laves phase variants.

Diffusion couples Co/TiCo and TiCo₃/TiCo were prepared by contacting two blocks of the single-phase materials, wrapping them into Ta foil, and heat-treating them in a pure Ar atmosphere at 1100 °C for 144 h and 168 h, respectively. In addition, eleven binary alloys with compositions between 4 and 50 at.% Ti were synthesized by levitation melting and heat treatments were performed at 800 °C for 500 h and 1100 °C for 50 h. As-cast and heat-treated samples were analysed by SEM-EDX, DSC and XRD.

The experimental results presented on this poster were obtained during a two-month summer-student internship of Maisam Merali at the Max-Planck-Institut für Eisenforschung.

Tuesday 9:00

(MPIE Colloquium)

Recent Advances in Heat-resistant Structural Material Development with Laves Phases at Oak Ridge National Laboratory

Yukinoro Yamamoto

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

This presentation provides an overview of recent developmental efforts at Oak Ridge National Laboratory (ORNL) on heat-resistant ferrous materials with Laves-phase strengthening for fossil-fired energy conversion systems. Laves phases are attractive as second-phase strengtheners in Fe-base alloys, including ferritic and austenitic stainless steels, since most of the Fe-rich Laves phases (Fe_2M intermetallic compounds, M: Nb, Mo, W, Zr, Ti, etc.) are thermodynamically equilibrated with BCC- or FCC-Fe solid solution. Because of the characteristics, relatively easy control of second-phase dispersion is expected through a traditional “solution-and-annealing” process combined with proper alloying additions. The thermal stability of the Laves phase precipitates at elevated temperature was found to be controlled and improved through combinations of multiple Laves-phase forming elements, which guides the alloy design and provides effective strengthening of high-temperature structural materials for the extended periods of time. Laves-phase precipitation in Fe-base matrix can be expected in relatively large composition/temperature ranges, which also allows designing the alloys with proper surface protections, such as chromia- or alumina-scale formation on the surface. This leads to proposing and designing new high-temperature structural materials to be used in extreme environments such as Advanced USC or supercritical CO_2 cycle applications. The presentation will also introduce various developmental efforts in Fe-base, Cr-base, and Cu-base alloys with Laves-phase strengthening at ORNL in the last decades. Research supported by the U.S. Department of Energy, Office of Fossil Energy, the Crosscutting Research Program.

Tuesday 10:20

Polytypic Transformations and Twinning in Laves Phases

Sharvan Kumar

School of Engineering, Brown University, Providence, RI, USA

Deformation of metals and alloys by dislocations gliding between well-separated slip planes is understood, but many crystal structures do not possess such simple geometric arrangements. Examples are the Laves phases with the AB_2 stoichiometry that are the most common class of intermetallic compounds and exist with ordered cubic and hexagonal structures. Here, I will discuss the structure of Laves phases, the “synchroshear” dislocation mechanism, and its ability to explain polytypic transformations; I will also present experimental results of stacking faults and dislocation cores in Cr_2Hf and Zn_2Mg . These show that this complex dislocation scheme does operate in this class of ordered intermetallics.

Tuesday 10:45

Atomic Arrangements at Planar Defects in C14 NbFe₂ Laves Phase

Christian H. Liebscher ¹, Michaela Šlapáková ^{1,2}, Sharvan Kumar ³, Frank Stein ¹

¹ Department of Structure and Nano-/Micromechanics of Materials, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany; ² Department of Physics of Materials, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic; ³ School of Engineering, Brown University, Providence, RI, USA

Advanced transmission electron microscopy (TEM) techniques are employed to explore atomic arrangements at planar faults in a C14 NbFe₂ phase with a Nb content of 35 at.%. Conventional TEM observations reveal a strong increase in the defect density by increasing the Nb content from 33 at.%, the stoichiometric composition, to 35 at.%. Atomic scale observations in an aberration-corrected scanning TEM (STEM) show that mainly two types of defects, extended and confined ones, are present in the Nb-rich material. Several polytypes of extended defects with a basal habit plane exist that extend over several hundreds of nanometers or more in width, but are only a few nanometers in height. The most intriguing observation for all these defects is that the layer arrangement resembles parts of the Fe₆Nb₇ μ -phase structure. Since both, the C14 Laves and μ -phase belong to the group of tetrahedrally closed-packed intermetallic phases, their crystal structures can be described in similar layer arrangements. In particular, the formation of characteristic Nb-rich layers seems to be one way for the system to accommodate the excess amount of Nb. Furthermore, confined defects are observed with both basal and pyramidal habit plane. The confined pyramidal defect with a width of only ~1 nm adopts a layer arrangement of exactly the Fe₆Nb₇ μ -phase. In contrast, the confined basal fault is only composed of a single type of Nb-rich triple layer causing a disruption in the stacking sequence of both C14 and μ -phase. The atomic scale arrangements of the different planar defect types are discussed in detail, also considering their role in compensating for the excess amount of Nb in the system.

Tuesday 11:10

Atomistic Investigation of Stacking Faults in Non-stoichiometric Fe-Nb Alloys

Ali Zendegani ¹, Michaela Šlapáková ^{1,2}, Christian Liebscher ¹, Sharvan Kumar ³, Thomas Hammerschmidt ⁴, Fritz Körmann ¹, Tilmann Hickel ¹, Jörg Neugebauer ¹

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The microstructure in structural materials plays an essential role for their mechanical properties. In Fe-Nb alloys a hardening via tetrahedrally close-packed (TCP) phases (e.g. Laves Fe_2Nb and μ Fe_7Nb_6) can be achieved. At the same time, various types of stacking faults not only occur during deformation but even appear in as-cast non-stoichiometric material. In the present work, we investigate the correlation of both features in a Nb-rich C14 Fe_2Nb Laves phase. For this purpose, density functional theory calculations are combined with thermodynamics concepts. Particular care has been taken to take relaxation effects and magnetic degrees of freedom into account.

By performing gamma surface calculations we resolve the atomic structure of these planar faults and show that they have a surprising geometrical complexity. Introducing a new thermodynamic framework allows us to compare the stability of planar faults (2D) with bulk phases (3D) in a convex hull diagram. The resulting diagram reveals that Nb-rich crystal structures next to basal and pyramidal stacking faults can become energetically more favorable than the nucleation of an epitaxially constrained μ phase. Excess Nb results thus in an enhanced formation of 2D stacking faults rather than forming 3D Nb rich precipitates in form of the μ phase. This unexpected finding allows a direct interpretation of recent HR-TEM studies on this materials system.

Tuesday 11:35

Evaluation between the Phase Stability and Geometrical Factor of C14-type Laves Phases

Ryosuke Yamagata¹, Masao Takeyama¹, Kyosuke Yoshimi²

¹ Department of Materials Science & Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo, Japan; ² Department of Materials and Science, School of Engineering, Tohoku University, Sendai, Miyagi, Japan

Introduction. Ferritic creep-resistant steels are the most candidate material for heavy wall components in next generation coal-fired power plants due to their low cost and low thermal expansion coefficient compared to austenitic steels and Ni-based alloys. Recently, Laves phase intermetallic compounds have been considered as one of effective precipitation-strengtheners in ferritic steels. Especially, Fe₂Nb Laves phase has attracted a great deal of attention because it has high thermal stability better than carbides [1]. Laves phase has three-types of crystal structure: i.e., hexagonal C14, cubic C15 and dihexagonal C36, and all they have topologically close-packed (TCP) structures. It is expected that there is close relationship between geometrical factors such as lattice parameter and axial ratio and phase stability. For the C15 structure, the effect of atomic size ratio on the formation enthalpies was studied in previous study [2]. However, there has been few reports about the phase stability of the C14 structure that mainly used in several heat-resisting materials. In this study, the structure of C14-type Fe₂Nb Laves phase equilibrated in a ferritic steel containing Al and Cr is refined by the Rietveld technique in order to relate the geometrical factors of the C14-type structure to the phase stability. The effect of Al and Cr substitution in Fe₂Nb on the geometrical factors is discussed.

Materials and Methods. The nominal composition of the alloys studied were Fe-(27-33.3) Nb-(0-16.67) Al or Cr at. %. These alloys were prepared by a conventional Ar arc-melting technique. Homogenization heat-treatment was carried out at 1300°C for 70 h under a vacuum of about 1.0×10^{-4} Pa. Structural analyses were performed by the Rietveld refinement. Powder X-ray diffractometry (XRD) was conducted using the Cu-K α radiation under the Bragg-Brentano focusing optical system. The Rietveld refinement was run on the TOPAS[®] software by Bruker AXS. The fundamental parameter method was applied on the profile function calculation. In order to measure micro-hardness, nano-indentation tests were carried out with the loading force of 10 mN.

Results and Discussion. From the results of the Rietveld refinement, the effect of Al and Cr substitution in Fe₂Nb on the lattice parameter and atomic coordinate of each element were clarified. The effective atom radii in each crystallographical atom site in Laves phase of $6h$ (Fe1), $2a$ (Fe2) and $4f$ (Nb) sites were numerically calculated from the lattice parameter and atom coordinate. The effective atom radius of two Fe-atom sites showed different values even though in case of the Fe₂Nb stoichiometric composition. From the results of packing ratio estimation using effective atom radii and unit cell volume, it was revealed that the packing ratio of Laves phase increased with Al and Cr addition. Therefore, it is suggested that the element-substitution behavior in C14-type Fe₂Nb Laves phase is based on the increase in

packing ratio. It was found that micro-hardness of the Laves phase increased with increasing the packing ratio. Because the hardness and melting-point have a positive correlation [3], it was expected that geometrical factors and phase stability also show correlativity in C14-type Fe₂Nb Laves phase.

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Tuesday 12:45

Multi-Center Bonding in Laves Phases by Position-Space Chemical Bonding Analysis

Alim Ormeci, Yuri Grin

Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

Laves phases contain a large number of intermetallic compounds and alloys which can be formed by elements from all over the periodic table. The reasons behind such a large variety in a single family of compounds have been the subject of many studies. Geometric and electronic criteria in various forms have been put forth to understand the formation of Laves phases. Along this line, we employ the method of position space chemical bonding analysis based on the electron localizability concept in order to shed light on the nature of atomic interactions in Laves phases. Our findings emphasize the significance of the electronegativity difference between the elements *A* and *B* of the Laves phase AB_2 [1]. Large differences mean large charge transfer, and in such cases stability is largely due to (i) the electrostatic interactions between the positively charged *A* cations and the anionic *B* networks, and (ii) the covalent *B* - *B* interactions within the anionic network. Small differences mean small charge transfer from *A* to *B* which supports the formation of multi-center bonds with 3 or more participating atoms, a feature observed not only in Laves phases, but in intermetallic compounds in general [1,2,3].

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Tuesday 13:10

Observations on the Composition Dependence of the c/a Ratio of Hexagonal Transition-metal-based Laves Phases

Frank Stein

Department of Structure and Nano-/Micromechanics of Materials, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

In the cubic crystal structure of a C15 Laves phase AB_2 , for both the larger A atoms as well as the smaller B atoms there is exactly one crystallographic site available (Wyckoff positions $8a$ and $16d$, respectively), and the smaller B atoms form a network of regular tetrahedra. However, in case of the hexagonal C14 Laves phase, the crystal structure offers two non-equivalent atom sites for the B atoms (Wyckoff positions $2a$ and $6h$) resulting in an intrinsic distortion of the B atom tetrahedra, which also manifests itself as a deviation of the lattice parameter ratio c/a from the ideal value 1.633 of the undistorted tetrahedra.

Especially in transition-metal-based systems, hexagonal Laves phase often have extended homogeneity ranges. When replacing B atoms by ternary additions of larger (smaller) C atoms, the lattice parameters a and c continuously and approximately linearly increase (decrease) as a function of the C content following the expectations from Vegard's law. Interestingly however, the c/a ratio behaves clearly non-linear and in many cases runs through a minimum value at intermediate C contents. Various examples will be given and are discussed in relation to details of the crystal structure.

Tuesday 13:35

Enthalpy of Formation of Laves Phases in Nb-Ni-Al and Nb-Cu-Al Systems

Qing Gu, George Kim, Wei Chen, Philip Nash (presenting author)

Thermal Processing Technology Center, IIT, Chicago, IL, USA

The standard enthalpies of formation of some Laves phases in Nb-Al-based ternary systems have been measured by direct synthesis calorimetry. The compounds measured were NbAlNi and NbAlCu over a range of composition. The measured enthalpies of formation (in kJ/mole of atoms) of Laves compounds in NbAlNi ternary system are: Nb_{0.33}Ni_{0.15}Al_{0.52} (-15.8 ± 0.6); Nb_{0.33}Ni_{0.20}Al_{0.47} (-14.6 ± 0.7); Nb_{0.33}Ni_{0.30}Al_{0.37} (-13.6 ± 0.6); Nb_{0.33}Ni_{0.40}Al_{0.27} (-13.2 ± 0.5); Nb_{0.33}Ni_{0.50}Al_{0.17} (-10.6 ± 0.4); and in NbAlCu ternary systems there are: Nb_{0.325}Al_{0.505}Cu_{0.17} (-15.7 ± 0.9); Nb_{0.32}Al_{0.45}Cu_{0.23} (-14.2 ± 0.8); Nb_{0.32}Al_{0.39}Cu_{0.29} (-13.2 ± 0.4); Nb_{0.32}Al_{0.33}Cu_{0.35} (-10.2 ± 0.1). Crystal structure of these compounds with Laves phase were verified by X-ray diffraction analysis. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy were used to examine the samples and determine phase composition. First-principles cluster expansion approach was employed to study the ordering of off-stoichiometric Cu₂-Ni-Sn Laves phases and the 0 K stability was also predicted from calculations. The compounds are typically extensions of binary Laves phases with significant solubility in the ternary system. This offers the opportunity to measure the enthalpy of formation over a range of composition providing insight into the alloying behavior.

Tuesday 14:25

Thermodynamic Modelling of Laves Phases in Chromium-based Systems below Room Temperature using ab initio Results

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Thermodynamic modelling of chromium-based Laves phases containing Ti, Zr, Hf, Nb and Ta above room temperature was published in our papers [1-3]. Using our values of Gibbs energies of elements extended to zero Kelvin temperature [4] we have compared Gibbs energies of chromium-based Laves phases for their stable modifications at 0 K temperature with the Gibbs energies of respective elements at 0 K temperature. On the basis of this, we demonstrate the stability and metastability of equilibrium Laves phases with respect to elemental constituents at 0 K.

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Tuesday 14:50

Modelling of Phase Equilibria in the Hf-V System below Room Temperature

Jana Pavlů^{1,3,2}, Jan Vřešťál^{1,2,3}, Urszula D. Wdowik⁴, Mojmír Šob^{3,2,1}

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Phase transformation from orthorhombic HfV₂ structure to cubic C15 Laves phase structure, occurring during heating at about 114 K, is well known. In this contribution, a thermodynamic description of this phenomenon is provided with the help of *ab initio* electronic structure calculations. We utilize the thermodynamic database extending the Scientific Group Thermodata Europe (SGTE) unary data to zero Kelvin [1] and demonstrate that this procedure may be also applied to intermetallic phases. The data from a recent thermodynamic assessment of the Hf-V system (valid for temperatures above 298.15 K) [2] are employed and extended to zero Kelvin by the same method as it was used for unary data [3]. Under the assumption of validity of harmonic approximation, thermodynamics of C15 and orthorhombic phase is described.

Acknowledgement:

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Tuesday 15:15

Phase Equilibria and Intermetallic Phases in Ti-Al-X (X = Cr, Mo) based Systems

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Titanium aluminides based on ternary Ti–Al–X (X = Cr, Mo) systems are promising materials for high-temperature applications because of their expected improved processability and high temperature oxidation resistance in comparison to the non-alloyed titanium aluminides. The phase equilibria in the Ti–Al–Cr system were studied experimentally with particular emphasis on the extension of the γ -Ti(Al,Cr)₂ Laves phase and on the homogeneity ranges of the β -(Al,Cr,Ti), γ -TiAl and τ phases. Equilibrium phase compositions were determined using electron-probe microanalysis (EPMA) and structure information were obtained from Rietveld analysis of X-ray diffraction (XRD) data to construct isothermal sections and assess solidus and liquidus surfaces.

The high-temperature phases originating from the binary Al–Mo system were successfully quenched and investigated using complementary experimental methods such as powder XRD, transmission electron microscopy (TEM), EPMA, scanning electron microscopy (SEM) and thermal analysis. It has been demonstrated that the β continuous solid solution and the binary high-temperature AlMo phase are one and the same phase. Moreover, the phase equilibrium studies at 1673 K showed the existence of the newly observed ternary τ phase which crystallizes in a face-centered cubic γ -brass related crystal structure. The crystal structure of τ was determined by additional single-crystal diffraction analysis from a crystal specimen. Thermal analysis measurements in combination with quenching experiments showed that the τ phase is a ternary extension of Al₆₃Mo₃₇ which is stabilized towards lower temperatures by the substitution of Mo by Ti atoms. Based on the obtained results, isothermal sections at 1673 and 1773 K, the liquidus projection and a partial Scheil reaction scheme were constructed.