Beyond Nickel-Based Superalloys IV

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Invited talk: Single-crystal mechanical properties of high- and medium-entropy alloys with the FCC structure

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High-entropy alloys (HEAs) comprise a novel class of scientifically and technologically interesting materials. Among these, the equatomic CrMnFeCoNi alloy with the face-centered cubic (FCC) structure and some of its derivative equiatomic quaternary and ternary alloys are noteworthy because its ductility and strength increase with decreasing temperature while maintaining outstanding fracture toughness at cryogenic temperatures. However, the origin of these excellent mechanical properties has yet to be understood clearly, because mostly of the luck of studies using their single crystals. In the present study, the plastic deformation behavior of single crystals of the FCC equatomic CrMnFeCoNi high-entropy alloy and its derivative quaternary (CrFeCoNi) and ternary (CrCoNi) medium-entropy alloys has been investigated in a temperature range of 10-1273 K. Deformation occurs via slip of the {111}<110> system exclusively in the whole temperature range for all alloys investigated. The CRSS values increase with decreasing temperature, especially below room temperature, so that the concept of ‘stress equivalence’ is obeyed for all alloys investigated. This is a clear indication that the strength of these alloys should be described by a mechanism based on solid-solution hardening. The CRSS values extrapolated to 0 K for polycrystals of equiatomic quinary, quaternary and ternary alloys are reported to be well scaled with the mean-square atomic displacement from the regular FCC lattice points (calculated based on density-functional theory). This seems also the case for the CRSS values at 10 K for single crystals of the present three alloys, although some modifications are definitely needed. Deformation twinning occurs on the conjugate system in the form of the Lüders type deformation in the later stage of deformation at low temperatures in all of the three alloys. The correlation between the twinning stress and the stacking-fault energy in these alloys will be discussed.

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On the bcc solid solution and its contamination with interstitials in refractory metal intermetallic composites (RMICs) and refractory complex concentrated alloys (RCCAs)

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Metallic UHTMs depend on refractory metals to meet property targets and thus are susceptible to interstitial contamination, which is particularly severe for their bcc solid solution(s) that can be "conventional", complex concentrated (CC) or high entropy (HE). The presentation will discuss (i) the stability of these solid solution (SS) types in B free and B containing alloys and (ii) the effect of contamination with oxygen on the yield strength σy and Young's modulus E of the SS.
"Conventional" SS can be Ti rich only in as cast alloys, and Ti rich SS is not observed in heat treated alloys. In B containing alloys the Ti rich SS is usually CC/HE. The CC/HE SS is stable after heat treatment in alloys with simultaneous addition of Mo, W with Hf, Ge and Sn. There is a strong correlation between the δ parameters of "conventional" and CC/HE SS with the B or the Ge+Sn concentration in the SS. Similarities and differences between relationships of other solutes in alloys with B or Ge+Sn addition will be noted and their implications for alloy design will be discussed.
The CC/HE SS has low $\Delta\chi$, VEC and Ω, and high ΔSmix, $|\Delta$Hmix$|$ and δ, and is formed in alloys that have high ΔSmix. These parameters will be compared with those of single phase SS HEAs and differences or similarities will be discussed. The parameters δss and Ωss, and VECss and VECalloy can differentiate between types of alloying additions and their concentrations and thus are key regarding the formation or not of CC/HE SS. Correlations between oxygen content and the parameters δ, $\Delta\chi$ and VEC show that the effects of interstitial contamination on properties can be understood and/or described with all three parameters. The B content of the SS correlates only with δ. The σy and E of the bcc SS increases linearly with its oxygen concentration and the change in yield strength and E due to contamination increase linearly with [O (at.%)]2/3.

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Experimentally screening the oxidation resistance and microstructure of refractory metals-based high-entropy alloys (RHEAs) with varying compositions

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High-Entropy Alloys (HEAs) based on refractory metals alloyed with light metals (RHEAs) show a promising combination of low density and high compression strength at high temperatures. Thus, the high potential of these alloy systems for high-temperature applications beyond nickel-based superalloys has risen extensive research interest.
In this work, AlMo0.5NbTa0.5TiZr, AlCrMoNbTi and AlCrMoTaTi were chosen as base RHEAs for variations in chemical compositions and experimental screening of isothermal oxidation resistance. In order to improve the three base alloys in terms of oxidation resistance and density, fractions of Al, Ti and Cr/Zr are systematically modified, respectively. Furthermore, the influence of Si additions is investigated. Thus, a total of 55 RHEAs are synthesised by vacuum arc melting, milling, spark plasma sintering (SPS), homogenisation heat treatment and surface preparation. Densities are determined by Archimedes method. The oxidation resistance of all RHEAs is screened gravimetrically by weighing before and after isothermal oxidation testing for 48 h at 1000°C in air. Selected promising RHEAs with highest oxidation resistances are investigated in more detail regarding phase composition, microstructure, mechanical properties and oxidation behaviour.
RHEAs are characterised using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), Vickers hardness testing and compression testing. Experimental findings are supplemented by thermodynamic data using CALPHAD simulations.

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Aluminum-based coating materials for application in high temperature (1300 °C) environments in glass molds

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Wear-resistant coatings are utilized in diverse applications to extend the lifespan of components. Specifically, for parts exposed to harsh conditions, the surface of the cost-effective base material must be reinforced to possess high resistance regarding abrasion and corrosion. In the context of glass molds, coating systems are critical in situations where they come into contact with molten glass or other aggressive and extremely hot substances. In industrial settings, a common issue is that melted glass adheres to the grey cast iron mold after a certain number of cycles. To address this problem, an Al-based alloy is applied to a substrate of lamellar grey cast iron through thermal spray processes.
Observations were made regarding the resulting microstructure of heat treatments on metallic coatings, as well as the development of intermetallic phases as well as the behaviour in high temperature glass melts at 1300 °C. Optical and scanning electron microscopy, with energy-dispersive x-ray spectroscopy, were used to analyse the microstructural characteristics of the coating. The coatings' mechanical properties, such as hardness and adhesion, were evaluated. Furthermore, we will present findings on the interactions between the coatings and glass melts.

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Alloy designs for high temperature Mo-base systems

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Recently, considerable effort has been devoted to the development of ultra-high temperature structural materials as alternatives to Ni-based superalloys to improve the energy efficiency of gas turbine systems. Among the several potential candidates, Mo-Si-B alloys have received much attention due to their high melting point and high temperature strength, but also have some remaining challenges to improve ductility, lower density and enhance environmental resistance. In the Mo-Si-B system microstructures with a Mo solid solution (Mo_{ss}) Mo_3Si and Mo_5SiB_2 (T_2) phases have been the focus of attention. However, the Si solubility in the Mo_{ss} phase diminishes the ductility and toughness. In order to address this issue, a new series of Mo-Si-B alloys in the $Mo_{ss}+T_2+Mo_2B$ three phase region has been designed to examine the effect of the lower Si solubility limit in the Mo_{ss} phase on the microstructure, hardness and oxidation behavior. The results showed that the Mo-Si-B alloys in the $Mo_{ss}+T_2+Mo_2B$ three phase region have higher fracture toughness and the same level oxidation resistance as alloys in the $Mo_{ss}+T_2+Mo_3Si$ three phase region. Selected additions of Al and Ti enable a density reduction to below 9 gm/cm^3, but also influence the oxidation behavior.

While refractory metal intermetallic alloys (RMIA) offer an attractive option to extend operational temperature capability, the processing of the RMIAs to manufacture dimensionally controlled shapes in a commercially cost-effective way is challenging. For RMIAs the directional solidification approach used for Ni base superalloys has serious difficulties. For example, there are very limited choices for suitable mold materials that are nonreactive with the alloy melt. The solidification path for large ingots in RMIAs involving intermetallic silicide and boride phases usually yields product phases that are not part of the equilibrium phase microstructure. Due to the high-temperature stability and sluggish diffusion in refractory metals, homogenization requires very high temperatures (>1500°C) and long annealing times (>1 day) that are not commercially cost effective. A conventional powder metallurgy processing approach for RMIAs involves several steps including the hot pressing of RMIA powders, high-temperature sintering, and then usually a hot isostatic press (HIP) treatment to achieve full density. Even with these multiple processing steps, it is difficult to produce complex shapes with accurate geometric control. To circumvent these challenges, an additive manufacturing (AM) route offers a new, rapid and effective strategy. With AM methods such as directed energy deposition (DED) and laser powder bed fusion (LPBF), alloying is accomplished by the melting and reactive synthesis of component powder mixtures to full density so that the size scale of any nonequilibrium solidification products is limited that facilitates post-alloying homogenization. This approach has been demonstrated to yield the fabrication of homogeneous alloys with well-defined shapes. Besides the successful use of AM, the guidance from computational thermodynamics to identify compositions that meet density, strength and ductility goals and the use of dimensionless numbers to guide the AM process has been essential to achieve fully dense component with the desired microstructures.

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Plenary talk: Fracture toughness of Mo-Si-B-Quartz Particulate Composites

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Multiphase Mo-rich Mo-Si-B alloys are potential candidates for high temperature applications owing to their favorable combination of high temperature strength, creep resistance and oxidation resistance. The inherent brittle nature of these alloys coupled with their low fracture toughness (<8 MPa √m) below 1000°C, limits their application in industry. The addition of α-quartz as particulate reinforcement to various multiphase alloys containing Mo solid solution, T2 and Mo2B resulted in increased fracture toughness values in the temperature range 200°C to 800°C. This improvement in fracture toughness behavior is also seen when quartz is added to two-phase alloys containing Mo solid solution and the T2 phase. Interrupted fracture toughness testing revealed that markedly higher loads were required to propagate the crack tip as compared to those required for the base alloy although the crack propagation mode did not visibly change. However, tensile tests above 900°C confirmed that the addition of quartz resulted in decreased macroscopic ductility as compared to the base alloy. These results will be presented and underlying deformation mechanisms will be discussed.

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Mechanical response of pesting-resistant Mo-Si-Ti alloys for high temperature applications

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Refractory metal based alloys exhibit intrinsically high creep resistance at anticipated application temperatures beyond 1100°C due to high solidus temperatures. In Mo-based alloy, however, Mo-rich phases usually form volatile MoO3 already at temperatures above 600°C, which leads to catastrophic oxidation. This keynote lecture addresses the mechanical behavior of novel Mo-Si-Ti alloys that successfully tackle this lack of oxidation resistance for the first time. We will provide a detailed analysis of the fundamental creep behavior at temperatures beyond 1100°C regarding: (i) the contribution of individual phases like Mo solid solution, hexagonal (Ti,Mo)5Si3 and tetragonal (Mo,Ti)5Si3 to strain and strain rate as a function of loading stress, (ii) their microstructural changes upon thermal and mechanical loading as well as the (iii) scaling behavior of creep response within a large range of alloy and phase compositions. Optimization potential regarding further alloy development is deduced from this analysis. Apart from the creep response, which is competitive especially when taking the densities of as low as 6.2 g/cm^3 into account, ductility remains challenging in alloys composed of high fractions of intermetallic phases, like the Ti- and Mo-rich silicides. Brittle-to-ductile transition temperature (BDTT) is hence discussed based on the fraction and 3D distribution of the constituting phases to assessing the engineering potential of the alloys. As the original alloy concept focused on the utilization of specific phase reactions to obtain fine-scaled microstructures in the as-cast condition (eutectic or solid state transformation processes), further development trends to improve the BDTT are proposed based on novel synthesis techniques.

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Analysis of V and Ti modified Mo-Si-B alloys

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Mo-Si-B alloys are attractive high-temperature structural materials due to their high melting point (above 2000°C), high-temperature strength, good oxidation and creep resistance. In order to reduce the density of Mo-Si-B alloys, Ti and V are promising candidates for alloying. Ti as well as V additions are found to cause strengthening of the alloy at intermediate and high temperatures without decreasing the ductility at room temperature. To understand the effect of Ti and V on the crystal structure of the constituents, the phase fractions of the multi-phase alloy and thus the mechanical properties at a range from ambient temperatures to 1100°C, we investigated different compositions of powder metallurgically (PM) processed Mo-Si-B-X (X=Ti/V) alloys. Due to PM processing oxygen cannot entirely avoided. If oxygen is not trapped in the lattice, it leads to oxide phase formation, and further contributes to strengthen the alloy by particle strengthening. The present investigations focus on the characterization of the constituents by SEM, EBSD and Atom probe tomography (APT), combined with Density Functional Theory (DFT) calculations. Based on the analyses, a conclusion can be drawn about the composition of the phases and the solubility of the elements in the phases. These in turn have an impact on the mechanical properties of the alloy, which will also be considered. For this purpose, compressive creep tests at temperatures over 1000°C and flexural bending tests are carried out, in order to evaluate the strength and fracture toughness of the alloys.

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Invited talk: Microstructural stability and elemental influence in refractory metal superalloys

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Refractory metal superalloys (RSA) have attracted considerable interest in recent years as a potential class of material that may supersede Ni-based superalloys in certain high temperature structural applications. These alloys offer an attractive combination of high melting temperatures, low intrinsic diffusivities, moderate densities, and microstructures that are reminiscent of Ni-based superalloys, with dispersions of small cuboidal precipitates. However, RSA microstructures are based on bcc and associated superlattice phases rather than the fcc and associated superlattice phases in Ni-based superalloys. The most widely studied RSA also comprise intermetallic matrices and solid solution precipitates rather than the inverse. This microstructural configuration leads to persistent concerns over ductility and toughness, despite the impressive high temperature mechanical strengths these alloys exhibit. Concerns also exist over their stability, as prolonged exposure to elevated temperature has been shown to lead to the formation of other intermetallic phases that are likely to compromise alloy properties. Therefore, for these alloys to progress to a level of maturity suitable for commercial consideration it is critical that an improved understanding is established of their governing phase equilibria, their microstructural stability under service representative conditions, and how they may be improved though compositional refinement.
In this presentation, studies that have sought to elucidate the origins of the microstructures of RSA will be discussed. These will build from investigation of alloys derived from ternary to senary systems. The results obtained highlight the role of key elements in controlling phase equilibria, microstructural development, and structural order. The stability of these alloys under long term thermal exposure will also be reviewed. The results are contrasted with thermodynamic calculations to assess the fidelity of existing databases to predict phase equilibria and the implications for future RSA development will be discussed.

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Diffusion of oxygen in γ-TiAl / α-Ti3Al intermetallic via isotope tracing

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Advanced intermetallic γ-TiAl based alloys are promising light-weight materials for high-temperature application and have been introduced into aero-engines as turbine materials. The current oxidation resistance performance of γ-TiAl at high temperature is inadequate thus an understanding of oxygen diffusion behaviour is pivotal. In this work, we heat-treated α2-Ti3Al lamellar imbedded in γ-TiAl based alloy at 700°C for 100 hours in an artificial atmosphere of isotopes, i.e. 18O instead of regular 16O. The atom probe results reveal that the 18O has the preference to enrich in the α2-Ti3Al phase. On the other hand, the γ-TiAl matrix contains almost no 18O from surface to interior. The concentration of 18O near surface can reach 7% and the diffusion depth is about 8 μm. In the γ-TiAl colony boundary, small plate-like α2-Ti3Al precipitates are formed probably because the O induced the phase transformation from γ-TiAl to α2-Ti3Al. O also diffuse though the interface between the colony and colony boundary, which could lead to the formation of oxidation at the interface. This work systemically investigated the diffusion and effect of oxygen in γ-TiAl / α-Ti3Al lamellar alloy, providing a better understanding of the oxidation behavior of TiAl alloy

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Utilization of discontinuous precipitation in selective electron beam melted nanostructured NiAl-(Cr,Mo) in-situ composites

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The very high melting point, low density, good thermal conductivity and excellent oxidation resistance of the intermetallic B2 phase NiAl makes it well suited for high temperature applications. However, the high-temperature strength and fracture toughness at room temperature show poor performance, which disqualifies the use of single-phase NiAl as a high-temperature material for structural applications. The addition of 28 at. % Cr and 6 at. % Mo to NiAl, however, results in an eutectic alloy that forms a two-phase, rod- or lamellar eutectic microstructure with significantly improved mechanical properties with directional solidification. Additive manufacturing techniques such as selective electron beam melting (SEBM) allow very high cooling rates, resulting in nanostructured composites with very small lamella spacing between the B2 NiAl and the bcc-Cr solid solution. This also leads to a very high density of interfaces, which could further improve the fracture toughness at room temperature.
In this study, dense and crack-free samples of eutectic NiAl-(Cr,Mo) in-situ composites were processed by selective electron beam melting using an Arcam A2. In the case of alloys with lower Mo content, rod-like structures resulting from discontinuous precipitates can be found in the additively produced composites. These discontinuous precipitates are triggered by in-situ heat treatment in the building chamber or ex-situ heat treatments. APT studies are used to further analyze and understand the formation of the nanostructured phases and the driving force behind this coarsening. This can then be used to adjust the SEBM process accordingly to either obtain fully discontinuously coarsened samples or prevent the formation.

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A2-B2 alloys based on the titanium-iron system

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The design of superlattice precipitate reinforced alloys can be extended beyond classical examples like the nickel-based superalloys by considering BCC-type systems. Titanium is an ideal candidate base element owing to its high specific strength and relatively high solubility for a range of transition metals, though the BCC (A2) phase is metastable at lower temperatures. Additions of iron serve to stabilise this phase and allow for reinforcement with superlattice precipitates by cooling from a high temperature single phase A2 field into a lower temperature A2 + B2 field, where age hardening can occur. However, the lattice misfit between these phases is relatively large in the binary system, which limits precipitate-matrix coherency. The misfit can be reduced by alloying with ternary elements, although, few Ti-Fe-X systems are well-characterised so the influence on phase equilibria is also not well-known. Here, we present the results of investigations into a range of Ti-Fe-X systems in order to characterise their phase equilibria and lattice constants, and thus assess their potential suitability for future structural alloy design.

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Invited talk: Formation of protective oxide scales on refractory high entropy alloys

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Refractory High Entropy Alloys (RHEA) are considered novel promising high temperature materials for structural applications at ultra-high temperatures primarily due to their attractive mechanical properties. While many RHEA suffer from poor oxidation resistance similar to that of pure refractory metals, some RHEA exhibit very good protectiveness which is attributed to the formation of rarely encountered complex oxides such as CrTa-based oxides. In this contribution, our recent results on the formation and growth of these oxides which exhibit high thermodynamic stability and slow growth kinetics, are presented. The effect of elements as well as their concentrations on the formation and growth of CrTa-based oxides on alloys within the system Ta-Mo-Cr-Ti-Al is discussed. It was found that Mo in concentrations below 20 at.% has no significant effect on the oxidation resistance, Ti beneficially supports the rutile crystal structure of CrTa-based oxides, Al facilitates the nucleation of Cr2O3 (required as a constituent of the CrTa-based oxide), while Cr and Ta represent the crucial elements in the formation of protective layers. In addition. the oxidation mechanism leading to the formation of protective CrTa-based oxide scales is suggested.

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Improvements in the oxidation resistance of ultra-high temperature niobium silicide-based alloys through boron and germanium additions

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Niobium silicide-based alloys are a promising new material to replace nickel-based superalloys for use in turbofan jet engines to improve efficiency, where material operating conditions can reach temperatures in excess of 1150°C. The main issue facing niobium silicide-based alloys is their poor oxidation resistance, which is primarily a result of the niobium solid solution phase (Nb_{ss}) having poor oxidation resistance and a high oxygen diffusivity.

Boron and germanium additions to refractory silicide systems (e.g. Mo-Si and Nb-Si based alloys for coatings) have been successful at improving oxidation resistance [1,2]. The goal of the present study is to improve the oxidation resistance through additions of both boron and germanium to a previously studied bulk alloy Nb-18Si-24Ti-5Cr-5Al (KZ5 [3]). As both boron and germanium can be substituted into amorphous SiO_2, the formation of an amorphous B-Ge-Si-O layer is a possible route to acceptable oxidation resistance [4].

The microstructures, oxides formed and phase compositions of a series of B and Ge containing alloys will be discussed based on EPMA-WDS, SEM-EDS and XRD results. Isothermal oxidation rates are calculated over 100 hours at 1000°C and 1200°C using thermogravimetry (TG). The oxides formed consist of mainly titanium and niobium oxides. No evidence of an amorphous silica layer is found at present under these conditions. However, the addition of boron and germanium in various amounts improves the oxidation rate at 1000°C and 1200°C significantly.

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Development and characterisation of PVD environmental barrier coatings for Mo-Si-based alloy

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Mo-Si-based alloys are being considered as high-temperature structural materials to replace Ni-based superalloys in the hot section of gas turbines due to their high melting point of over 2000°C and superior mechanical properties. As a result, significantly higher operating temperatures could be achieved in comparison to state-of-the-art Ni-based superalloys. However, their oxidation behaviour is inadequate, as MoO3 evaporates at temperatures below 1000 °C and rapid oxide growth occurs at temperatures above 1000°C. By applying protective coatings against oxidation and water vapor corrosion, so-called environmental barrier coatings (EBC), a sufficient resistance of the alloys against environmental threats over a wide temperature range can be ensured.

In this work, a multisource sputter coater was used to deposit a four-layer PVD EBC system on Mo-Si based alloys. Oxidation protection was provided by a dual layer coating system containing a graded Mo-Si interlayer to compensate for differences in the coefficient of thermal expansion (CTE), and a pure Si top layer to serve as a reservoir for the desired protective thermally grown oxide layer of SiO2. Ytterbium monosilicate (YbMS) is well known for excellent water vapor resistance and provides a CTE close to that of Mo-Si-based alloys. In order to restore the thermodynamic equilibrium between the oxidation protective Si layer and the YbMS, another intermediate layer of ytterbium disilicate (YbDS) was deposited. The EBC system on different Mo-Si-based alloys was tested at 800 °C and 1200 °C in laboratory air where it successfully improved the oxidation resistance. The emphasis was on the chemical reactions and diffusion processes at the interfaces of the coating system, which were analysed by scanning and transmission electron microscopy as well as electron dispersive spectroscopy, respectively. Due to the specific design of the multi-layer coating, all interfaces were stable, but some interdiffusion occurred mainly between the protective dual layer coating system and the alloys by forming an interdiffusion zone after prolonged oxidation. In addition, phase formation was evaluated using high temperature X-ray diffraction techniques.

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High temperature oxidation of high entropy alloy CrTaTiAlMo with varying ratios of Cr and Ti

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Refractory high entropy alloys are promising candidates for structural, high temperature oxidation resistant, materials [1]. The equiatomic quinary alloy CrTaTiAlMo and the influence of its Ta and Ti content on the alloys oxidation behavior and microstructure has previously been investigated [2, 3].
In this work, the influence of a varying ratio of Cr to Ti content on the oxidation mechanisms is investigated. Adjusting the Cr to Ti ratio could influence oxygen diffusion by decreasing the number of oxygen vacancies in possibly protective CrTaTiO6 layers due to the higher valence of the Ti4+ cations compared to Cr3+ cations [3]. The oxidation behavior of the equiatomic alloy CrTaTiAlMo was compared to 13at.%Cr-Ta-27at.%Ti-Al-Mo and 27at.%Cr-Ta-13at.%Ti-Al-Mo, providing 1:2 and 2:1 atomic ratios of Cr to Ti. The samples were exposed to Ar-H2O atmospheres at temperatures up to 1000°C. The formed oxide layers were analyzed by XRD and in cross section by SEM, EDS and EPMA to provide knowledge about their oxidation kinetics.

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Oxidative protective coatings - recent advances

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Oxidative protective coatings have been gaining attention in the recent years for high temperature applications. Two novel Co-Ni-Al-Mo-Ti alloys with Ta and Nb additions were aluminized using the halide activated pack cementation process. In all cases, a 3-layer surface modification was noted after aluminizing. The outer layer consisted of two phases, i.e., AlCo and Al7Co2Ni in all cases. No obvious differences were noted in the morphology of the aluminized layers in the two different alloys for the same process conditions.

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Invited talk: Solidification paths and phase diagram of ZrC-added Mo-Si-B alloys

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Mo-Si-B alloys are expected to be candidates for ultra-high-temperature materials because of their high melting points and excellent high-temperature strength [1,2]. The alloys have as constituent phases the Mo5SiB2 (T2) phase, which has excellent high-temperature strength, and Moss (molybdenum solid solution) phase, which forms a toughening mechanism. However, the Moss phase has a high density. Therefore, if the amount of Moss phase is increased to improve the fracture toughness of the alloy, the density of the alloy will increase. Recently, Yoshimi et al developed ZrC-added Mo-Si-B (MoSiBZrC) alloys to reduce the density and reported their microstructure and mechanical properties [3]. They suggest that the continuity of the ductile Moss phase in the alloys contributed to the improvement of room-temperature fracture toughness [3]. Therefore, microstructure control is important to improve mechanical properties such as room-temperature fracture toughness. The purpose of this study is to investigate the solidification paths of the constituent phases that contribute to the mechanical properties of the alloys and to construct a phase diagram based on the solidification paths of the constituent phases. To achieve this objective, information on the phase transformation temperatures and their microstructural changes is necessary. Therefore, we evaluated phase transformation temperatures by ultra-high temperature thermal analysis using blackbody radiation and microstructural changes associated with phase transformation by analyzing the microstructures of rapidly solidified alloys prepared by electromagnetic levitation (EML) in a static magnetic field [4]. The composition of MoSiBZrC alloys, expressed as a pseudoternary system consisting of Mo, Mo5SiB2 (T2), and ZrC, was studied for four alloys containing 10 mol% ZrC (Mo/T2=77/13, 75/15, 70/20, and 65/25 in mol%). A comparison of the solidification process of MoSiBZrC and MoSiBTiC systems will also be discussed.

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SL 6 - 2

Microstructure and material properties of rapidly-solidified MoSiBTiC alloy

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Microstructure control is essential for the development of MoSiBTiC alloys. In the MoSiBTiC alloy with a composition of Mo-5Si-10B-10Ti-10C (at%), solidification causes the following three eutectic reactions in order of increasing temperature: Mo solid solution (Mo_{ss}) + TiC, Mo_{ss} + Mo_5SiB_2 (T_2) +TiC, and Mo_{ss} + T_2 + Mo_2C. Extreme microstructural refinement is expected in the eutectic regions due to rapid solidification processes such as 3D additive manufacturing. Therefore, the microstructural evolution of the MoSiBTiC alloy by rapid solidification and its effect on material properties are investigated in this study.

A Mo-5Si-10B-10Ti-10C (at%) alloy was produced by a conventional arc-melt technique in an Ar atmosphere and then rapidly solidified by tilt-casting into a rod-shaped copper hearth of about 4 mm in diameter and 60 mm long. Microstructure was relatively homogeneous up to about 50 mm from the bottom of the hearth. The microstructure near the surface of the rod in contact with the copper hearth was almost a ternary eutectic phase of Mo_{ss} +T_2 + TiC, one order of magnitude finer than the as-cast MoSiBTiC alloy reported in our previous work. In the center of the rod, the microstructure was slightly coarsened but still finer than the as-cast MoSiBTiC alloy. Coarsened Moss + TiC eutectic phase was occasionally observed.

Vickers hardness values increased drastically above 1000 Hv due to the rapid quenching effect. They increased from the center toward the surface, ranging from about 1100 Hv to 1300 Hv. Interestingly, the oxidation resistance of the rapidly solidified MoSiBTiC alloy at 1100 °C was dramatically improved, probably due to the microstructure refinement effect. However, the fracture toughness value was found to be about 8 $MPa{\cdot}m^{1/2}$, which was less than half of the cast and heat-treated MoSiBTiC alloy previously reported. Heat treatment and composition optimization will further improve the performance of the rapidly solidified MoSiBTiC alloy.

SL 6 - 3

Fabrication of MoSiBTiC alloy powders using freeze-dry pulsated orifice ejection method and plasma spheroidization for additive manufacturing

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MoSiBTiC alloys are promising candidates for next-generation ultrahigh-temperature materials due to their excellent high temperature strength and high fracture toughness at room temperature. Laser powder bed fusion (L-PBF) is one of the innovative processing technologies to fabricate MoSiBTiC alloys with complex components. When MoSiBTiC alloys are processed by L-PBF, a major problem is the difficulty in producing spherical powders. Therefore, a novel technique, freeze-dry pulsated orifice ejection method (FD-POEM), was developed to fabricate the spherical MoSiBTiC composite powders for L-PBF. The FD-POEM powder was found to have a narrow size distribution, a uniform distribution of elements and a high laser absorptivity [1,2]. However, due to the mesh porous structure and low strength of the FD-POEM powders, it is likely that they were fractured during the powder recoating process. In this study, MoSiBTiC powders prepared by FD-POEM were tried to improve the strength of the FD-POEM powders by plasma spheroidization (PS).

The Mo, Si, TiC and MoB powders with sub-micron size were selected as raw materials. The FD-POEM process was employed to prepare Mo-Si-MoB-TiC composite powders. The PS treatment was performed using high frequency induction melting in a mixed gas of argon and hydrogen. The powder size distribution and morphology of the FD-POEM powders were determined using an image analyzer coupled to an optical microscope. The microstructure of PS powders was observed using a scanning electron microscope (SEM) with an energy-dispersive spectrometer (EDS).

Spherical Mo-Si-MoB-TiC composite powders with a mesh-like structure were obtained using FD-POEM. After the PS treatment, the morphology of FD-POEM powders was kept spherical and showed a smooth surface. In addition, the FD-POEM powders was shrunk and the average particle volume reduced by approximately 90%. The PS powders were in situ alloyed, and mainly consisted of Mo, Mo3Si, T2, and TiC phases. The oxygen content was significantly decreased after the PS treatment.

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SL 6 - 4

Printability of Mo-Si-B alloys by laser-based additive manufacturing

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Mo-Si-B alloys are promising materials for challenging ultra-high temperature structural applications, e.g. turbine blades in gas turbines. Different fabrication methods for such high melting alloys were investigated in the past, e.g. conventional powder metallurgical processes and solidification processes. However, there are restrictive constraints using such methods, e.g. the size and the geometry of the semi-finished products as well as the essential post-machining to produce the final components.

The use of additive manufacturing processing would enable a more efficient and resource-saving process, though, the processing by additive or generative techniques is very challenging due to the ultra-high melting point beyond 2000°C and the complex solidification behavior of three constituents. This presentation shows the properties of gas atomized Mo-Si-B powders tailored for laser-based additive manufacturing processes, i.e. Laser Powder Bed Fusion and Directed Energy Deposition. The printability of Mo-Si-B powders is demonstrated and a typical layer-wise microstructure evolution is observed in the builds. Pre-heating was found to be mandatory for the production of crack-free samples with very low residual porosity. The compact builds are investigated in terms of their microstructural evolution and the thermal stability. Important mechanical properties like hardness, brittle-to-ductile-transition temperature and creep resistance at temperatures around 1100°C will be presented. Furthermore, the oxidation behavior of the alloys at different temperatures is comparatively discussed with regard to powder metallurgically processed Mo-Si-B materials.

SL 7 - 1

Invited talk: Bcc-Superalloys - bcc refractory metals reinforced by ordered-bcc intermetallic precipitates

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The microstructure template of a disordered matrix reinforced by ordered-intermetallic precipitates offers a potent design strategy for high temperature materials, enabling strength alongside damage tolerance, which has been central to the success of fcc nickel-based superalloys. Such a strategy is equally applicable to bcc-based systems, which offer advantages of increased melting point, lower cost, and/or lower density. However, whilst bcc-superalloys based upon a refractory metal, Ti, Cr or Fe matrix, strengthened by ordered-bcc intermetallic precipitates are possible, further research and development is need for them to become a commercial reality beyond nickel-based superalloys.

In this talk, opportunities for bcc-superalloys systems will be discussed, from binaries to ternaries and more complex alloys, including Refractory High Entropy Superalloys. It will then discuss our latest developments in tungsten-based bcc-superalloys, beta-Ti superalloys and chromium superalloys. Prospectives will be given for the onward development of the bcc-superalloy concept for application in nuclear fusion, Gen-IV fission, gas turbines and concentrated solar power.

SL 7 - 2

Is there a niche for modified platinum group metals in aeroplanes?

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Platinum group metals (PGMs) are mostly fcc and have high melting points. Although not having the highest melting point of the PGMs, platinum has been used as a component in coatings and also as spacers during turbine manufacture. Although too heavy and too expensive to be considered as a bulk material for the high temperature applications in aeroplanes, some platinum-based alloys do have interesting properties. The fcc structure gives good mechanical properties, including reasonable ductility and formability, and the excellent chemical stability of platinum gives excellent oxidation resistance and excellent corrosion resistance, which have been used to advantage in coatings, as well as in the very aggressive glass-making industry (especially for high quality glasses).
Much work has already been done on PGM alloys, mostly concentrating on platinum and iridium, and many alloys have aluminium to produce the strengthening precipitates, which means the alloys are similar to the well-established, but temperature limited, nickel-based superalloys. However, Pt3Al has at least three different structures (unlike Ni3Al which only has only the cubic structure), although the desirable high temperature cubic phase can be stabilised by different alloying additions. Alloying additions could also potentially increase solid solution strengthening and increase the melting point. There are other interesting properties of Pt-based alloys which have not been explored, including shape memory affects, and these could increase the potential for applications.

SL 7 - 3

Investigation of the Superlattice Phases Formed in Ta72Ru28

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The Ta-Ru binary phase diagram has not been fully investigated, but shows potential for a two-phase region of A2+B2. Given the high melting points of both Ta and Ru, such an alloy would have the potential for high temperature strength. A Ta72Ru28 alloy was arc melted and investigated in the as-cast and aged (at 1000°C) states. The as cast alloy was composed of A2 and B2, albeit not in a superalloy-like morphology. A third phase was found in the aged alloy, which has not been reported before, and which is also a coherent superlattice phase of the Ta BCC matrix. The structure of this phase was found to be consistent with the tetragonal Cr2Al prototype structure, with lattice parameters of (a, a, 3a), where a is the Ta BCC lattice parameter.

SL 7 - 4

Investigation of mechanical properties of alloys based on refractory metals at high temperatures

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The demand for energy-efficient internal combustion engines, in particular gas turbines, requires the use of high-temperature materials with the highest possible operating temperature. Alloys based on the refractory metals chromium, molybdenum and niobium are promising candidates for such materials.
In this work the test results of selected mechanical properties of refractory metal-based alloys are presented. The shear and tensile moduli of polycrystalline chromium and molybdenum-based alloys are examined and compared with those of common nickel-based superalloys. In particular, the temperature dependency of these material constants is discussed in more detail.

SL 8 - 1

Invited talk: Refractory complex concentrated alloys as potential candidates for high temperature applications beyond Ni-based superalloys

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Refractory complex concentrated alloys (RCCAs) have recently brought much attention as promising candidates for high-temperature structural applications, beyond Ni-based superalloys. Due to high melting temperatures, refractory metals and alloys can be used at temperatures much above 1000°C showing exceptional strength retention and creep resistance. However, high density, high brittle-to-ductile transition temperature and inferior oxidation resistance limit the applications of many conventional refractory alloys based on a single element. The RCCA concept provides much higher flexibility for the selection of alloy compositions for improved properties. In particular, RCCAs with reduced densities, considerably improved oxidation resistance, room temperature ductility and high-temperature strengths have recently been identified. Here we report the results of our analysis of the effect of melting temperature, phase composition, chemical composition and density of currently reported RCCAs on their room temperature and high-temperature mechanical properties. Oxidation behavior is also briefly overviewed. Based on this analysis we make several conclusions, which may be useful for the future development of high-temperature RCCAs.

SL 8 - 2

Synthesizing refractory high-entropy alloys (RHEAs) in the Al-Cr-Mo-Ta-Ti material system by means of laser metal deposition (LMD)

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Refractory high-entropy alloys (RHEAs) are considered to be one of the most promising candidates for high temperature applications beyond the temperature range of Ni- and Co-based superalloys. However, the oxidation resistance of many RHEA is still. Gorr et al. developed strategies to design intrinsically oxidation resistant RHEAs in the Al-Cr-Mo-Ta-Ti alloy system. Despite of this progress there remains the huge challenge of poor manufacturability that results from strong room temperature embrittlement and limits the synthesis of these alloys to a few grams in the lab-scale.

Laser metal deposition (LMD) utilizing in situ alloying of different pre-alloyed or elemental powders is a very reliable experimental tool for the high-throughput screening and fabrication of HEAs. Utilizing this approach, in the current work, the synthesis of the AlXCrYMoTaTi RHEA system by LMD is explored covering a wide compositional range from 0 to 15 at% Al and Cr content. Gradient and single composition wall structures were produced by in-situ mixing of MoTaTi, Al and Cr powders using an in-house developed cladding system. The changes in microstructure with increasing Al and/or Cr content was analysed in the as-built condition by means of analytical scanning electron microscopy (SEM). Additionally, the evolution of sample micro-hardness with increasing Al and Cr content was determined.

The obtained results show that LMD is a suitable synthesis method for the processing of relatively brittle AlXCrYMoTaTi RHEA system that allows crack free processing up to a hardness of 600 HV. Generally, in the as built condition, a dendritic structure consisting of Ta and Mo-rich dendrites and Ti-, Al- and/or Cr-rich interdendritic regions is formed. With increasing Al and Cr content a transition from the disordered bcc A2 phase to a mixed structure consisting of disordered A2 and ordered B2 phase is observed. This change in phase composition is accompanied by a substantial increase in hardness.

SL 8 - 3

Additive manufacturing of FeNiCoCr high-entropy alloy with improved combination of mechanical properties

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High-entropy alloys, with improved combination of mechanical properties, are excellent structural materials for industrial applications. However, most high-entropy alloys are fabricated using traditional synthesis approach, which is typically a multiple-step processes and time-consumable. In this work, via in-situ alloying, we successfully additively manufactured a non-equiatomic FeNiCoCr high-entropy alloy, which possessed a great combination of mechanical properties. This alloy presented an ultimate tensile strength of 561 MPa with 41% elongation. The deformation mechanisms were revealed via in-situ electron backscattered diffraction testing and molecular dynamics simulations. High density dislocations and deformation twins were the main reason for this great combination of mechanical properties.

SL 8 - 4

A New CALPHAD database for high temperature applications

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Thermo-Calc Software is widely used in Alloy Design and frameworks for Integrated Computational Materials Engineering (ICME). The strength of the CALPHAD-based methodology behind Thermo-Calc, is that it enables accurate interpolation between and extrapolation beyond experimentally known chemistries, allowing the exploration of new alloys, and the means to produce them in terms of processing parameters.

A new CALPHAD database for Ultra-High Temperature Materials, TCUHTM1, was first released by Thermo-Calc Software in the end summer of 2022, together with Thermo-Calc version 2022b.

The database is aimed towards applications such as hypersonic and space vehicles, commonly experiencing temperatures above 3000 °C. Example materials used for such extreme applications are borides, nitrides and carbides of refractory elements. The first version of the database includes the elements B, C, Hf, N, Si, Ta and Zr, with all binary systems and 26 ternary systems assessed.

Capabilities of the database are demonstrated through examples such as phase diagrams, thermodynamic and thermochemical properties, phase equilibria of multicomponent alloys and Scheil solidification simulations of multicomponent alloys.

Future developments of the database are also discussed.

SL 9 - 1

MoSiB(Ti) by powder metallurgy and PBF-EB

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In the MoSiB system the Berczik triangle has been established to describe a three phase field to form tough and strong high temperature materials. Synthesizing the material by powder metallurgy or additive manufacturing offers both new prospects and challenges towards the formation of phases and microstructure. Especially at HIPed PBF-EB processed specimens a 4 point bending strength exceeding 1200 MPa at temperatures between 800°C and 1000°C could be achieved. This is attributed to the fine microstructure following the rapid solidification. Since also plastic deformation was achieved the formation of a coherent metallic matrix phase is very likely to have occurred. SEM and EBSD investigations were performed to support this.

The powder metallurgic samples were densified by spark plasma sintering following heat treatment including HIP. For this route also titanium containing samples were prepared. Adding titanium may lead to a different phase field favoring the formation of the Mo5Si3 phase over Mo3Si phase promising better creep resistance and oxidation resistance. Additionally Ti5Si3 participates may increase the ductility of the alloy by reducing the silicon content in the molybdenum solid solution and at the grain boundaries. SEM microstructure observations showed stripe like features of alternating Mo and Mo5Si confirming the eutectoid decomposition of the Mo3Si phase. However no annealing window could be found to fully decompose that phase.

SL 9 - 2

Strengthening of additively manufactured Me-Si-B by Y2O3

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Structural materials are faced with enormous requirements concerning strength, wear resistance, but also crack tolerance. In the last decade's refractory metals and their alloys were more and more considered as potential alloys for these requirements.

Besides others, Mo-rich Mo-Si-B alloys are in the focus of research on innovative turbine materials, as they provide high strength at ambient temperatures and satisfactory fracture toughness as well as high thermal resistance and improved creep resistance [1]. Simulations and comparative experimental assessments against Ni-base superalloys already demonstrated the outstanding performance of Mo-Si-B alloys [2,3]. V-Si-B alloys, following a similar alloying concept, was found to offer enormous potential as well, although at a lower temperature regime (up to 1000°C) in comparison to Mo-Si-B alloys (up to 1300°C) [4]. Both refractory Me-Si-B (Me = Mo, V) alloys show up with good ductility and fracture toughness for a microstructure consisting of hard and creep resistant silicide phases surrounded by a more ductile solid solution matrix [5,6]. Conventional processing methods, like powder metallurgy and ingot metallurgy, were already investigated for Me-Si-B alloys [1,4–6] and currently we are working on the establishment of additive manufacturing (AM) for this class of materials [7,8].

However, one limitation on the use of the above-mentioned materials is the notably decreasing creep resistance at higher temperatures. The high strength level at ambient temperatures, which is improved by grain refinement, is not stable at temperatures above 0.3*Tm. Me-Si-B materials for the use in high temperature application suffer from creep damage, that is mainly observed in the solid solution phase, while the silicide phases provide improved creep resistance.

Oxide dispersion strengthening (ODS) is known to increase the high temperature materials strength and creep response of metallic materials. The application of the ODS concept on additively manufactured alloys, like Fe- and Ti-Al-based alloys was already shown [9,10]. The feasibility of the ODS approach in structural Me-Si-B materials produced by additive manufacturing is still unexplored. In this study, a new approach of additive manufacturing of Y2O3-doped Me-Si-B powder is presented. This approach combines the oxide dispersed strengthening (ODS) mechanism and additive processing of innovative intermetallic materials. Homogenously distribution of Y2O3 particles in the pre-alloyed Me-Si-B powder material was achieved by means of a short grinding process in a planetary mill. Undoped Me-Si-B powders are used as reference material. Bulk samples were consolidated via direct energy deposition (DED) as a method for AM and examined regarding microstructure, hardness and compression tests.

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SL 9 - 3

Experimental investigation of the isothermal section of the V-rich V-Si-B system at 1400°C

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The three-phase Vss-V3Si-V5SiB2 alloy represents a new candidate material for high-temperature structural applications due to the high melting temperature and good creep resistance provided by the hard intermetallic phases V3Si and V5SiB2. Describing the isothermal section is necessary in order to develop appropriate heat treatment and sintering processes.
In this work, eight alloy compositions were investigated to characterize the isothermal section of the V-Si-B system at 1400°C. Samples were produced via arc-melting and heat treated at 1400 °C for 100/200/300 h and furnace-cooled (within 3 h below 200 °C) in high vacuum (1.5·10−5 mbar). Their microstructures were characterized using scanning electron microscope, energy-dispersive X-ray spectroscopy (EDS), electron backscatter diffraction (EBSD) and X-ray diffraction (XRD). The phase area fraction determined by EBSD and the phase volume fraction, which was determined using the phase composition measured by EDS in combination with the phase molar volume measured by XRD, were used to confirm the sample equilibrium state thereby reflecting the isothermal section of the V-rich V-Si-B. Compared to the isothermal section at 1600 °C [1], the V5SiB2 single-phase field at 1600 °C is partially replaced by the V8SiB4−V5SiB2 coexistence line at 1400 °C. Accordingly, it divides the V5SiB2−V3Si two-phase phase field at 1600 °C into the V3Si−V5SiB2−V8SiB4 and V3Si−V5SiB2 phase fields at 1400 °C. Furthermore, the V5SiB2 phase of the Vss−V3B2−V5SiB2 and Vss−V3Si−V5SiB2 three-phase fields at 1600 °C is replaced by the novel V8SiB4 phase.

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SL 9 - 4

Microstructure and mechanical properties of V-Si-B alloys with chromium additions

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The V-Si-B system has gained scientific interest as a new low-density, refractory metal-based structural intermetallic alloy system. The alloy design is strongly influenced and driven by the developments in the field of Mo-Si-B alloys and shares some interesting structural and microstructural features. Very recently, the formations of ternary eutectic VSS-V3Si-V5SiB2 microstructure has been reported which contains the same isomorphous phases as the ternary eutectic in the well-studied Mo-Si-B system: a refractory metal-based solid-solution phase (MoSS or VSS) and the two intermetallic phases with either an A15 (Mo3Si and V3Si) or a D8l (Mo5SiB2 and V5SiB2) structure. However, while the Mo-Si-B-based ternary eutectic shows some oxidation resistance due to its intermetallic character, oxidation of the V-based eutectic is an even more serious issue. To address this problem, different amounts of Cr were added to an eutectic V-Si-B alloy to study the microstructural influence on the ternary eutectic reaction, the phase stability as well as the mechanical and oxidation properties as a function of Cr concentration. Alloys with Cr additions between 5 – 30 at.% were fabricated by conventionally arc-melting and were analyzed in the as-cast state or heat-treated at 1400°C for 100 hrs.

The present study is focused on the compressive stress-strain behavior of ternary eutectic V-Si-B alloys with 10, 20 and 30 at.% Cr additions. Compression tests were performed using an electro-mechanical universal testing machine and a constant crosshead speed corresponding to an initial (engineering) strain rate of 10-3 s-1. The yield stresses were determined by the 0.2% offset method. The temperature dependence of its compressive yield stress between room temperature and 1000°C was investigated in the as-cast and annealed state (1400°C for 100 hrs) and compared to the Cr-free ternary eutectic alloys V-9Si-6.5B as well as V-Si-B alloys taken from the literature.

SL 10 - 1

Investigation of different MC-carbides for particle strengthening of Co-Re-based alloys

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Co-Re-based alloys are currently investigated as potential high temperature materials with melting temperatures beyond those of Ni-based superalloys. Their attraction stems from the binary Co-Re phase diagram, exhibiting complete miscibility between Co and Re whereby the melting temperature steadily increases with the Re-content. Thus, depending on the Re-content one can tune the melting temperature between that of pure Co (1455°C) and that of pure Re (3186°C). Current investigations focus on Re-contents of about 15 at.%, which makes melting with standard equipment still feasible. Besides solid solution strengthening due to the mixture of Co- and Re-atoms, strengthening by TaC precipitates turned out to be attractive, see e. g. [1]. However, as there are a number of potential MC-type carbides and given significant differences in their lattice parameters, it is presently unclear whether TaC is the best choice. To address this open issue, TiC and HfC particles are investigated here in addition to TaC. It will be demonstrated that TiC and TaC are the best options to achieve a reasonably homogeneous distribution of fine precipitates whereas HfC and various Co-Hf phases precipitate as coarse particles in the Co-Re-Cr-Hf-C system. TaC and TiC are then investigated further. Transmission electron microscopy is used to analyze the shape of the precipitates and their orientation relationship to the matrix. Compression tests at elevated temperatures of these TaC and TiC containing variants and the particle-free matrix are performed to assess strengthening contributions and mechanisms. Based on these findings it will be concluded that TiC and TaC are equally suited for precipitation strengthening of Co-Re-based alloys.

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SL 10 - 2

Strain rate dependent formation of local phase transformations in a CoNi-base superalloy

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In the last decade, segregation to planar defects in superalloys has become the focus of attention. Segregation of certain elements to stacking faults reduces their energy, allowing shearing of γ'-precipitates at lower stresses. The segregation tendency depends on the alloy composition and can promote a local phase transformation that can significantly improve the mechanical properties of superalloys. While most studies have been performed on crept specimens, experimental data on the influence of time on segregation-assisted plasticity are lacking. Recently, the temperature-dependent defect structure of a complex CoNi-based superalloy was analyzed in detail. A transition from shear by APB-coupled dislocation pairs to shear under the formation of stacking faults with increasing temperature was reported.
In this work, the strain rate dependency of a complex single-crystalline CoNi-base superalloy ERBOCo-4 (Co-32Ni-8Al-5.7W-2.8Ti-1.8Ta-6Cr-0.4Si-0.1Hf) is investigated. The evolution of the defect structure from interrupted compression tests at temperatures from 800°C to 950°C and varying strain rates between 10-2 s-1 and 10-6 s-1 is analysed with conventional transmission electron microscopy. At higher temperatures and/or lower strain rates a change in deformation mechanism towards shearing under the formation of stacking faults is reported. This change in the deformation mechanism is coupled with an increase in the yield strength and leads to higher work hardening rates. However, the different strain rates also lead to variations in the defect structure. HRSTEM studies have shown that a local phase transformation occurs at superlattice extrinsic stacking faults in a slower deformed sample with a strain rate of 10-5 s-1. This is in contrast to previous results on a specimen deformed with a strain rate of 10-4 s-1, where there are no local phase transformations leading to the formation of microtwins. The chemical composition is analysed by HRSTEM-EDS for both specimens, which shows significant differences in the W content along the different planar faults. Due to the low diffusion rate of W, a higher concentration of the element can be measured for the slower deformed sample. In the case of the faster deformed sample, the W content is not sufficient, impeding the formation of a local phase transformation.

SL 10 - 3

High-Cr CoNi-based superalloys with superior high-temperature microstructural stability, oxidation and mechanical properties

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Compared to widely used Ni-based superalloys, the potential for higher temperature capability is expected in γ′-strengthened Co-based superalloys due to the higher melting temperature. In addition, γ′-strengthened Co-based superalloys usually have a higher sulfide melting temperature than Ni-based superalloys, which is beneficial for long-term service in an environment containing sulfur, such as industrial gas turbines. However, due to the complexity of the actual service environment, the design of complex multi-component commercial superalloys has always been challenging due to the interaction of multiple elements and stringent requirements for various properties. In this study, an integrated approach to designing the high-component (>7) γ′-strengthened Co-based superalloys with well-balanced properties is developed by combining the diffusion-multiples and machine-learning models. High-Cr novenary CoNi-based superalloys with superior comprehensive performance were screened for industrial gas turbines working at temperatures above 900°C. After that, the microstructural stability, oxidation property and some high-temperature mechanical properties were evaluated. The microstructural stability of the optimal high-Cr novenary CoNi-based superalloys is better the than that of conventional Co-Al-W-based superalloys and comparable to some Ni-based single crystal superalloys containing Re at 950°C. Continuous Al2O3 layers form at 1000°C, and its oxidation resistance is superior to Ni-based cast superalloy MarM247 and PWA1483. In terms of mechanical properties, the yield strength of the optimal novenary CoNi-based superalloy is higher than that of superalloy PWA1483, and its compressive creep resistance is comparable to some typical Ni-based superalloys at 950°C. This work shows a good potentiality of the high-Cr CoNi-based superalloys for the application in industrial gas turbines and provides a guideline for the compositional optimization of γ′-strengthened Co-based superalloys.

SL 10 - 4

Formation of an onion-like two-phase structure and its effect on mechanical properties of refractory-metal based alloys

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It is found that an onion-like two-phase spherical shell structure is formed in refractory-metal based alloys during a heat-treatment for spinodal decomposition. SEM-FIB observation revealed it has a 3D structure composed of several shell-structures each of which are single phase accumulating alternatively from core to outside. Because of its spherical shape, isotropic mechanical properties are expected. It is noteworthy that once a propagating crack in the alloy reaches the onion-like structure, it is effectively deflected along a brittle phase layer or two-phase boundary in the structure and finally stopped at a ductile phase layer. 3D phase-field simulation revealed that the onion structure is formed with a certain initial condition which might be introduced during solidification.

SL 10 - 5

In-situ characterization of the temperature-dependent γ/γ′ lattice misfit and the creep behavior of single-crystalline superalloys with varying Co/Ni-ratio using X-ray diffraction

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The sign of the constrained γ/γ′ lattice misfit is a major difference between Co- and Ni-base superalloys. In this study, the temperature-dependent γ/γ′ lattice misfit of the single-crystalline model alloy series Ni–Co–9Al–8W–8Cr (at.%) ranging from pure Ni- to pure Co-base superalloys was investigated by in-situ high-resolution X-ray diffraction (HRXRD) up to 1000 °C. Moreover, the direction dependent γ′ lattice parameter evolution during the early stages of compressive creep along the [001] crystallographic direction at 900 °C and 250 MPa in the Co-9Al-8W-8Cr (at.%) was studied using in-situ high-energy X-ray diffraction (HEXRD). The Co/Ni-ratio strongly affects the sign of the lattice misfit and its temperature-dependent behaviour. The Ni-rich alloys show a negative lattice misfit at room temperature that becomes more negative at higher temperatures. In contrast, the Co-rich alloys exhibit a positive lattice misfit at room temperature that slightly tends towards zero upon heating. The γ′ lattice parameter along the [001] direction, i.e. parallel to the axis of the external applied compressive stress during creep testing, was found to stay nearly constant throughout the test duration during in-situ creep test of the pure Co-base superalloy. In contrast, the lattice parameter of the γ′ phase along the [010] direction increases with increasing creep duration. The different evolution of the γ′ lattice parameters can be attributed to the loss of coherency between the γ and γ′ phase during creep deformation. Since the sign and magnitude of the lattice misfit at high temperatures strongly affect the resulting coherency stresses within the alloys and thus mechanical properties, knowledge of the temperature-dependent lattice misfit is crucial for future superalloy development.

SL 11 - 1

Invited talk: Pushing the boundaries - development of Cr-Si-alloys for aggressive high temperature environments

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Cr-rich Cr-Si-based alloys are promising candidates for high temperature structural materials. They allow increase of efficiencies of high temperature applications compared to commonly used Ni-based alloys due to: (i) their higher melting point, thus a potential increase in working temperature by 100 – 200°C, (ii) lower densities (~82%) and (iii) higher worldwide resources of Cr and Si (factor 102).
Beside Si, elemental additions of Ge, Mo, and Pt were considered. All investigated Cr-Si alloys (Cr > 84 at.%) develop a two-phase microstructure, consisting of A2 Cr solid solution matrix and strengthening A15 (Cr,Mo)3(Si,Ge,Pt)-phase precipitates. A major drawback of the use of Cr-alloys at temperatures > 1000°C are their low oxidation and nitridation resistance. Low fractions of alloying elements such as Ge, Mo, and Pt were found to improve these during exposure to air at temperatures between 1050 to 1350°C.
Recently, the application boundaries of Cr-Si-alloys were further investigated with respect to harsh high temperature conditions. Tensile creep tests in air were performed to investigate the interaction between mechanical load, oxidation, and nitridation. In terms of corrosion resistance, Cr and Cr-Si-alloys were exposed to a hot corrosion type I environment (Na2SO4 deposit) for 20 h at 900°C and a Cl-containing salt melt (molten NaCl-KCl-MgCl2) for 20 h at 700°C demonstrating a very good resistance even in such harsh environments. Additionally, a high resistance towards metal dusting attack, another very aggressive form of high temperature corrosion related to H2-production, at 620°C under 18 bar pressure (ac,RED = 358) was proven. The respective performance varies with additions of ternary and quaternary alloying elements and thereby can be optimized by alloy design.

SL 11 - 2

Heat-resistant Cr-alloys - microstructure and creep performance

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A two phase alloy of Cr, bcc, solid solution matrix strengthened by a Cr3Si, A15 ordered, intermetallic phase was investigated with the goal of achieving an alloy with properties beyond nickel-based superalloys. In comparison to the well-known Ni-base superalloys, the Cr-Si alloys may enable higher working temperatures and lower densities slightly above 7 g cm-3. In addition, Cr is the only refractory metal which intrinsically builds an oxide scale suitable for protecting the alloy from oxidation. Si improves the oxide scale formation even further as well as a high temperature strength by precipitation of an intermetallic phase Cr3Si. We observed that the addition of further alloying elements such as Mo, Ge, and Pt leads to an improvement in creep properties (Mo), oxidation resistance (Ge), and nitridation resistance (Pt) by maintaining the two-phase microstructure. Creep tests were conducted at temperatures at 980°C and higher and reveal promising results. The microstructures, scales, and reaction products are investigated by XRD, SEM, EPMA and Image Analysis.

SL 11 - 3

Experimental determination of phase diagrams of the Cr–Si and Cr–Ta binary systems

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Refractory metal-based alloys have attracted much attention for novel high-temperature materials beyond Ni-base superalloys. Cr has a potential as high-temperature material because of its higher melting point and lower density than Ni. Cr–Ta alloys strengthened by the Cr2Ta Laves phase have been reported to exhibit excellent high-temperature strength and fracture toughness, but improvement of the oxidation resistance is required. On the other hand, Cr–Si alloys have better oxidation resistance. Besides, they can show a higher specific strength at high temperatures than Ni-based superalloy [1]. Although an accurate phase diagram is important for alloy design, reliable experimental data of phase equilibria are limited for refractory metals due to difficulty of the experiments at high temperatures. In this study, the phase diagrams of the Cr–Si and Cr–Ta binary systems were experimentally determined for future development of Cr–Si, Cr–Ta, and Cr–Si–Ta alloys with good mechanical properties and oxidation resistance.

The experiments were performed with attention to the heat treatment conditions and temperature accuracy at high temperatures up to 2000°C. Cr–Si and Cr–Ta alloys were heat-treated using an electrical heating furnace below 1400°C and a high-frequency induction heating furnace with a two-color pyrometer above 1500°C. Equilibrium compositions were measured by EPMA/WDS. DSC and DTA were also used to determine the transformation temperatures. Temperature calibrations for heat treatment and DSC/DTA measurements were performed by using the melting points of various pure elements.

The phase diagrams were determined in the whole composition range of the Cr–Si [2] and Cr–Ta systems, except for the liquidus and solidus lines on the Ta-rich side. In particular, the solubility range of some intermetallic compounds was revised against the reported phase diagrams.

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SL 11 - 4

Microstructure and heat treatment of chromium-based Cr-x(x=10-40)Mo-8Si alloys developed for service temperatures above 1100°C

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Increasing the maximum service temperature of structural materials is often coupled to an increased efficiency e.g. in gas turbines. Since the state-of-the-art materials (Ni-based-superalloys) reached their application limit at around 1150°C, alloys that are based on high melting refractory metals gain more attention [1]. Amongst them chromium offers a high availability, reasonable cost and density, making it a suitable candidate. However, pure Cr shows undesired high temperature corrosion mechanisms, such as nitridation and the formation of volatile species [2]. Previous work has shown that the addition of silicon strongly improves the corrosion resistance of Cr-based alloys above 1000°C. In the range of 5-13 at.% Si, a precipitation-hardenable structure of a Cr solid solution matrix (A2) with intermetallic Cr3Si (A15) precipitates is formed [3]. The A15 phase shows high creep resistance and nitridation and oxidation resistance. Some recent studies suggest that molybdenum, as an additional alloying element, can equally substitute for Cr in both phases and can promote a refined microstructure as well as solid solution hardening. It also increases the creep resistance of the A15 phase further and improves the nitridation resistance of the A2 matrix [2-4].

This work studied the influence of Mo content (10-40 at.%) on the microstructure of arc melted Cr-xMo-8Si (at.%) alloys. The ‘as cast’ state was compared to the post-annealed state. Phase composition(s), morphology as well as the room temperature hardness were determined and compared. Corrosion test were performed in air keeping the alloys at 1200 °C for 50 h. Based on the results a promising composition range was chosen and an adjusted two-step heat treatment for post annealing was developed, to establish a homogenous microstructure composed of an A2 (Crss) matrix with finely, regularly distributed intermetallic A15 (Cr3Si) precipitates.

An outlook on planned future work is given including upscaling via powder metallurgical route and extensive mechanical testing to identify a suitable application window for the alloy.

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SL 12 - 1

Plenary talk: Effect of selective alloying on strength, toughness and oxidation resistance of cast and annealed niobium silicide based multiphase refractory intermetallic alloys

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Niobium silicide based multiphase alloys have drawn significant attention in recent years for use in the hot-end components of aero-engines at temperatures beyond the operating range for nickel-based superalloys, due to the high melting point, along with impressive strength retention and oxidation resistance at high temperatures. In the multiphase Nb-Si based hypereutectic alloys, the high temperature strength retention is contributed by the presence of Nb_5Si_3, whereas toughening depends on volume fraction, size and morphology of the Nbss phase. On addition of 20 at% Ti and subsequent annealing at 1500oC, the fracture toughness of selected compositions has increased by as much as ~75% and ~63%, respectively with ~14 MPa$\sqrt{m}$ being recorded for the annealed Nb-12Si-5Mo-20Ti alloy. Further, on 3 at% Zr addition, the fracture toughness of the hypereutectic Nb-19Si-5Mo-20Ti is increased by 35.5% to 15.9$\pm$0.2 MPa$\sqrt{m}$. The toughening is ascribed to the formation of non-lamellar eutectic with coarse Nbss phase, which contributes to crack path tortuosity by bridging, arrest, branching and deflection of cracks. The compressive yield stress decreases with increase in test temperature, with the hypoeutectic alloys exhibiting higher strength retention indicating the predominant role of solid solution strengthening of Nbss by alloying with Mo, Ti and Zr. Alloying with Mo, Ti and Zr lowers the solubility and diffusivity of oxygen in the Nbss phase, which has led to the formation of thinner, compact and defect-free oxide scales in the Nb-Si alloys with hypereutectic compositions. The microstructural evolution due to the addition of optimum amounts of Mo, Ti and Zr, and its role in simultaneous improvements in strength, fracture toughness and oxidation resistance by a significant amount will be discussed.

SL 12 - 2

Manufacture of Nb-silicide based alloys via field assisted sintering technology

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Manufacture and upscale of Nb-silicide based alloys is a known challenge [1]. Advanced manufacturing methods have been proposed to overcome defects from conventional casting and allow greater control over the microstructure. Field Assisted Sintering Technology (FAST) is an effective sintering method for many different powdered materials, including metals and alloys [2]. It is capable of consolidating to high densities whilst requiring relatively low temperatures and processing times, due to simultaneous application of heat and pressure, along with rapid heating rates. FAST is therefore a suitable technique for production of Nb-silicide based alloys from powders, and has been shown to give fully dense material whilst eliminating any casting defects and generating a more refined microstructure [3].
In this work we present results from manufacture of 60 mm diameter Nb-Si based alloy produced using FAST. Powder was produced by first pre-alloying elements using arc melting, followed by crushing and ball milling under inert atmosphere. 90-100g of powder was consolidated in a 60 mm diameter graphite mould at 1500°C to produce a monolith.
Microstructure and phase analysis of the As-cast and FAST Nb-Si alloy using SEM/EDX and XRD will be presented along with assessment of mechanical properties. Production of samples with graded compositions (e.g. substrate and coatings) using FAST will be discussed.

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SL 12 - 3

Heat treatment and mechanical property of Additive manufacturing of refractory Nb alloy

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Refractory metal C103(89Nb-10Hf-1Ti) alloy with siliconized coating shows extraordinarily resistant to heat. Accordingly, C103 alloy has been applied for in jet engine afterburner components and the rocket engine nozzle. These components are expected to further improve their performance need to complex shape with cooling channel. For this point, additive manufacture of refractory Nb alloy is suitable to aerospace applications.

SL 12 - 4

Effects of lamellar orientation on the room temperature tensile properties of directionally solidified Nb-Si based ultrahigh temperature alloys

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Nb-Si based ultrahigh temperature alloys possess low densities, high melting point and good high temperature mechanical properties, which are expected to be employed as the next generation aviation turbine engine blade materials to be used at temperatures of 1200-1450°C. However, due to their poor room temperature fracture toughness and high temperature oxidation resistance, Nb-Si based ultrahigh temperature alloys can still not meet the requirements of high temperature structural applications in aerospace fields. Directional solidification process can effectively modify the microstructures and improve the comprehensive mechanical properties of Nb-Si based ultrahigh temperature alloys. Lamellar orientation of the eutectic structure has a significant effect on mechanical properties, so it is necessary to determine the most suitable lamellar orientation and crystallographic orientation of the constituent phases for the best mechanical properties of Nb-Si based ultrahigh temperature alloys, and therefore regulate the lamellar orientation in the turbine blades through adjusting the directional solidification process. Besides, the deformation mechanism will depend on the lamellar orientations of the directional eutectic structure of Nb-Si based ultrahigh temperature alloys.

The cylindrical bars with 30 mm in diameter and 90 mm in height of Nb-Si based ultrahigh temperature alloy were directionally solidified at a melt temperature of 2050°C and a withdrawal rate of 100 μm/s. The directionally solidified microstructure is mainly composed of primary γ-(Nb,X)5Si3 and Nbss/γ-(Nb,X)5Si3 eutectics. The eutectics present both petal-like and radially aligned lamellar morphologies in the cross-sections. The crystallographic orientations of Nbss and γ-(Nb,X)5Si3 in lamellar eutectics along the vertical axis of the directionally solidified samples are $<111>_{Nb}$ and $<0001>_{\gamma}$ respectively. The crystallographic orientation relationship is $<111>_{Nb}//<0001>_{\gamma}$ and $\{110\}_{Nb}//\{10\bar{1}0\}_{\gamma}$.

The tensile specimens with 0, 15, 30, 45, 60 and 90° angles between the Nbss/γ-(Nb,X)5Si3 eutectic lamellar orientations and the tensile axes of the specimens were electro-discharge machined from the directional solidified cylindrical bars with 30 mm in diameter and 90 mm in height. The influence of the eutectic lamellar orientation on the room temperature tensile properties and the deformation mechanism were then revealed. When the angles between the orientation of lamellar microstructure and the direction of stress axis are 0° and 15°, both the average ultimate tensile strength and elongation value are very high, and are in the range of 615.3-624.2 MPa and 2.7-3.4 %. The specimens with 60° angle between the Nbss/γ-(Nb,X)5Si3 lamellar orientation and the tensile axis possess the highest ultimate tensile strength and elongation, and they are respectively 676.7 MPa and 3.7 %. When the included angles are 30° and 45°, the average ultimate tensile strengths and elongation values have been lowed obviously, and they are respectively 435.7-450.5 MPa and 2.3-2.5 %. When the angle is 90°, both the average ultimate tensile strength and elongation value are the lowest, and they are respectively 355.0 MPa and 2.1 %. The deformation and fracture mechanisms under different lamellar orientations have been clearly illustrated.

SL 13 -1

Pressureless sintering of Mo-based metal-matrix composites

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Metal-matrix composites (MMCs) are advanced materials and widely used in various fields of industry, where high physical, mechanical and functional properties are of vital importance [1]. Mo-based alloys show great potential for ultrahigh-temperature applications because of their high melting points, high stiffness, and low coefficient of thermal expansion. However, the insufficient strength at elevated temperatures, low-temperature brittleness and poor oxidation resistance are the main concerns for Mo-rich alloys in practical use [2]. Toward this end, fabricating Mo-based MMCs reinforced with multi-phase Mo-Si-B material and Ti5Si3 ceramic particles have been aimed to solve the above-mentioned problems. Moreover, using of powder metallurgy technology makes it possible to obtained a uniform distribution of reinforcing particles in the molybdenum matrix as well as a fine-grained MMCs microstructure, which is a necessary condition for high mechanical characteristics.

The activated pressureless sintering (PLS) of MMCs (Mo- matrix reinforced with multi-phase Mo-9Si-8B particles as well as Ti5Si3 ceramic particles) by the addition of Ni was applied. The influence of technological parameters of PLS (temperature and holding time) and the concentration of the reinforcing particles were investigated. Based on the analysis of the microstructure and phase composition the main mechanisms of sintering and formation of the composite microstructure were established. The mechanical properties of dense composite materials were also studied.

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SL 13 - 2

Alloying strategies and optimization of powder metallurgically processed Mo-Si-B alloys

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The refractory metal-based Mo-Si-B alloys have long been considered as the most promising candidates for replacing nickel-based superalloys in the aerospace and energy sector, due to their outstanding mechanical properties and good oxidation characteristics of the Mo silicide phases. However, the oxidation behavior of these alloys still remains a critical issue, since catastrophic oxidation failure occurs locally at the Mo solid solution phase, especially at temperatures between 600 and 800°C.
The addition of vanadium leads to a significant density reduction compared to conventional ternary Mo-Si-B alloys, which is even lower than the density of a state-of-the-art nickel-base superalloy CMSX-4. It has been found that the composition Mo-40V-9Si-8B has the best set of properties with respect to normalized mechanical strength and ductility. In this work, a milling study of mechanically alloyed Mo-40V-9Si-8B powder will be carried out first with the aim to optimize the powder metallurgical processing route. In the next step, 2 at. % and 5 at. % titanium will be added, substituting both the molybdenum and the vanadium in all constituents, which improves the stress-strain properties even further. The mechanically alloyed powder obtained from the total of five milling studies will then be characterized as a function of milling time. Due to the high affinity of titanium for oxygen, it is believed that titanium may act as a getter for dissolved oxygen in Mo-V-Si-B alloys and thus contribute to improve ductility as well as to minimize internal oxidation. The analytical methods to determine the milling progress include SEM analysis (microstructure and EDS), XRD analysis (vanadium content of solid solution phases as well as their phase fractions, lattice constant and microstrain), oxygen measurements, microhardness measurements and laser diffraction (particle size). The aim of these studies is to obtain a better understanding of the influence of other alloying elements in powder metallurgically processed Mo-V-Si-B alloys and, based on this, to further optimize the material in terms of mechanical properties and oxidation resistance. Based on the results obtained from the milling studies, the alloy with the best property profile will be selected, which will then represent a new, improved starting material for the subsequent coating experiments.

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Micromechanical modelling of near-eutectic Mo-Zr-B and Mo-Hf-B alloys

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Refractory metals with high melting points are promising candidates to replace Ni-based superalloys in high-temperature applications. Mo-based alloys strengthened with boride phases show promising results in terms of mechanical properties. Such properties are ensured due to the combination of ductile solid solution and creep-resistant reinforcement phases.
In this work, the creep behavior of Mo-Zr-B and Mo-Hf-B near-eutectic alloys are described using a micromechanical mean-field elastoplastic model. The only inelastic phase is considered to be a Mo-rich solid solution. All boride phases are assumed to accommodate strains elastically. All the elastic constants of phases are estimated using density-functional theory. The plastic behavior of the Mo-rich solid solution is approximated using the pure Mo data with a correction due to solid-solution strengthening.
The redistribution of stresses and strains between phases is investigated during the creep loading of material. The influence of the lamellar spacing and morphology of non-eutectic borides is studied in terms of the influence on the high-temperature strength of the above-mentioned materials. The minimal creep rates are compared with experimental values, available in the literature.