The effects of Zr and La$_2$O$_3$ additions on the microstructural and mechanical properties of a Mo-6Si-5B alloy

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Abstract. In order to improve the application-related properties, as fracture toughness, creep response and oxidation behavior of Mo-Si-B alloys, certain alloying strategies can be applied. Promising alloying partners like Zr and La$_2$O$_3$ may help to enhance the compressive and flexural strength of Mo-Si-B materials. Accordingly, a combination of 1 at.% Zr and 0.5 wt.% La$_2$O$_3$ was chosen in order to improve the characteristic properties of a powder metallurgical (PM) Mo-6Si-5B alloy. The influence of Zr and La$_2$O$_3$ on the phase distribution and the mechanical properties will be discussed by means of three-point-flexure at room temperature as well as uniaxial compressive creep tests at elevated temperatures (> 1000 °C). Compared with other PM Mo-Si-B alloys the present Zr-La$_2$O$_3$-strengthened alloy shows highly improved fracture toughness at room temperature.

1 Introduction
Mo-Si-B alloys have been identified as high-potential materials in numerous comprehensive research studies and are thus promising candidates to replace nickel-based superalloys which are limited in their operating temperatures to a maximum of 1150 °C. Prior investigations show that certain application-related properties, as fracture toughness, creep response and oxidation behavior of those Mo-Si-B alloys [1–3], can be directly affected by their chemical composition according to the ternary phase diagram [4–6] and via different existing manufacturing processes [7–10].

Properties of Mo-Si-B alloys consisting of both brittle as well as ductile phases (silicides and Mo solid solution phase, respectively), are significantly affected by their volume fractions. The thermomechanical stable silicide phases Mo$_3$Si and Mo$_5$SiB$_2$ are mainly responsible for the excellent creep and good oxidation resistance of this group of alloys [2,3,7]. In contrast, the bcc Mo solid solution phase (Mo$_{ss}$) is responsible for the fracture resistance and brittle-to-ductile transition temperature [1,11–13].

Therefore, the Mo$_{ss}$ phase is a decisive microstructural constituent since it was found to affect the properties of multi-phase Mo-Si-B alloys significantly by its volume fraction, homogeneity and chemical composition [14]. Accordingly, it was reported that Mo-Si-B alloys consisting of a continuously formed Mo$_{ss}$ matrix phase with homogeneously distributed silicides (Mo$_3$Si and Mo$_5$SiB$_2$) show a balanced relation between the application-related properties [7]. With regard to further improvement of the crack and fracture tolerance, recent research focused on avoiding the embrittlement of the Mo$_{ss}$ phase by interstitial as well as solid solution elements. The most critical embrittling element is Si which is dissolved up to concentrations about 3 at.% in technical alloys, reported in [7,13,15].

A promising alloying strategy was developed to improve the ductility and fracture toughness of the Mo$_{ss}$ phase by alloying with Zr, which is mainly due to its getter effect on the detrimental oxygen and the suppressing of Si segregation as well as the formation of ZrO$_2$ particles and the deflection of cracks
at the phase boundaries [1,11,16,17]. Furthermore, an improvement of hardness and strength was reported due to the formation of nanoscale zirconia particles affecting the microstructure by dispersion strengthening, stabilization of a very fine-grained microstructure as well as increased grain and phase boundary cohesion due to reduced interstitial contamination [18]. Another positive effect was found by alloying with La$_2$O$_3$, which predominantly caused grain refinement and particles dispersion strengthening improving both compression and flexure strength of Mo-Si-B alloys [19].

Combining the promising effects of Zr and La$_2$O$_3$, this article reports on the impact of alloying additions of 1 at.% Zr and 0.5 wt.% La$_2$O$_3$ on the mechanical properties of a Mo-6Si-5B alloy. Microstructural investigations, room temperature three-point-bending tests using notched samples and compressive creep tests at 1093 °C will be applied in order to evaluate the effects on the application-related properties as fracture toughness as well as high temperature creep response. In addition to the reference alloy Mo-6Si-5B, the alloys Mo-9Si-8B and Mo-9Si-8B-1Zr were used to evaluate the creep performance, since these provide similar microstructures and promising creep properties.

2 Materials and Methods

For the present investigations, a Mo-6Si-5B material was alloyed with 1 at.% Zr and 0.5 wt.% La$_2$O$_3$, which in the following will be mentioned as the Mo-6Si-5B-1Zr-La$_2$O$_3$ alloy. The material was processed by a powder metallurgical (PM) route that included a mechanical alloying (MA) step to achieve fine-grained and chemically homogeneous powder particles. MA was carried out under protective (argon) atmosphere in a planetary ball mill (Retsch PM 400) with a speed of 200 rpm followed by a CIP-sinter-HP process, detailed described elsewhere [7,20]. For reasons of comparison a similarly processed alloy Mo-6Si-5B was used [7,20].

For microstructure investigations the samples were wet-ground from 500 down to 1200 grit and the specimen surface was finished by polishing with 3 µm and 1 µm diamond suspension. The microstructural analysis was applied by means of X-ray diffraction measurements using an XPert X-ray diffractometer (PANalytical) with Bragg-Brentano geometry and Co-$K_{al2}$ radiation ($\alpha_1 = 1.789$ and $\alpha_2 = 1.793$) and scanning electron microscopy (SEM-FEI ESEM XL30 FEG equipped with EDS, while images were typically obtained in the BSE mode. Quantitative phase analysis was performed using the Rietveld method with the Topas Academic V5 program package (A.A. Coelho, Topas Academic V5, Coelho Software) and the crystal structures of Mo, Mo$_2$Si, and Mo$_5$Si$_2$ as starting parameters, detailed described elsewhere [21].

The room-temperature fracture strength was applied performing three-point-bending tests on notched bending specimen with dimensions of 2 mm x 2 mm x 18 mm (DIN EN ISO 23146). In a first step, the ground and polished bending specimen were provided with a pre-notch using electrical discharge machining (EDM), ending up with a notch geometry of 0.8 mm in depth and less than 0.2 mm in width. A "sharp crack" with typical depth of 200 µm and a tip radius of around 10 µm was produced using a self-built cutting device equipped with a razor blade working with 1 µm diamond paste. In order to control the notch depth and tip-radius, the samples were examined at defined intervals (15 – 20 min) using an optical microscope.

Fracture toughness measurements were then performed applying a minimum number of five samples having similar notch base radii of around 10 µm. Three-point flexure was realized using a microtest cell (Materials Testing Nano Tomography Version 3.2, Deben) at ambient temperature with a load rate of 0.5 mm/min after preloading with 2 N. The determination of fracture toughness was carried out as described elsewhere [21]. The compressive creep behavior was determined on EDM-cut samples with dimensions of 2 mm x 2 mm x 3.5 mm, tested under constant true stress using a Zwick electromechanical testing device equipped with a Maytec furnace at a temperature of 1093 °C. This temperature was chosen to ensure the comparability to other Mo-Si-B alloys tested at 2000 °F (= 1093 °C).
3 Results and Discussion

3.1 Microstructural investigations
Representative micrographs of the PM alloys are shown in Figure 1. In case of the Zr-La$_2$O$_3$-added alloy, a finer-grained microstructure can be observed with an average grain size of 0.7 µm, which represents a reduction of 56% compared with alloy Mo-6Si-5B [7] having an average grain size of 1.6 µm.

According to X-ray diffraction (Figure 1c and [7]), both alloys exhibit the typical three-phase microstructure of Mo$_{ss}$-Mo$_3$Si-Mo$_5$SiB$_2$. However, the additions of 1 at.% Zr and 0.5 wt.% La$_2$O$_3$ are of a very low quantity in order to detect them via XRD measurements.

A part from that, EDS element mapping for the elements O, Zr and La, depicted in Figure 1d, illustrate that the black particles within the microstructure of Mo-6Si-5B-1Zr-La$_2$O$_3$ are mainly ZrO$_2$. However, also a small amount of SiO$_2$ particles might be present since not every individual oxygen-containing
3.2 Impact of Zr- and La2O3-alloying on the room temperature fracture toughness

Figure 2a shows a comparison of the fracture toughness of different Mo-Si-B alloys arranged by their increasing amount of continuous or discontinuous Mo6ss phase. The room temperature fracture toughness of the intermetallic phases with 1.5...3 MPam1/2 [22] is significantly lower than for pure Mo (24 MPam1/2 [15]). Therefore, fracture toughness values of Mo-Si-B alloys as reported in literature are typically in between 6 and 16 MPam1/2.

In general, depending on the chemical composition (Si and B concentration) and the manufacturing process a continuous Mo6ss or silicide matrix (discontinuous Mo6ss) forms. As illustrated in Figure 2a, the fracture toughness of Mo-Si-B alloys can be divided into two groups: The alloys having a silicide matrix (black symbols - discontinuous Mo6ss) exhibit typical fracture toughness values between 6 and 7.4 MPam1/2 and alloys having a continuous Mo6ss matrix (open symbols) provide values between 11 and 18.8 MPam1/2. The Mo6Si-5B-1Zr-La2O3 alloy has a nearly continuous Mo6ss matrix phase and the fracture toughness of 18.8 MPam1/2 exceeds the values for this type of alloys given in the literature. This is assumed due to the following reasons: (I) the high amount of Mo6ss phase, (II) and its continuous distribution, (III) the very fine microstructure of Mo6ss phase after alloying with Zr and La2O3 which according to Schneibel et al. [23] also affects the fracture toughness and (IV) reduced embrittlement of grain boundaries by gettering the detrimental oxygen accompanied with the formation of ZrO2 [17].

As depicted in Figure 2b alloy Mo6Si-5B-1Zr-La2O3 shows a mixed fracture mode of predominantly transgranular fracture in Mo6ss but also intergranular fracture, the latter within the silicide phases. Metallographic observations of cracked samples show interactions between the Mo6ss phase and the intermetallic phases, i.e. crack deflection and crack interception which were also identified in other fine-grained Mo-Si-B materials with homogeneous microstructures, e.g. in [1]. These effects are due to a high probability of the interaction of the crack path with the ductile Mo6ss phases.
3.3 Effects of Zr and La₂O₃ on the creep properties of Mo-6Si-5B
The high temperature creep performance of the Mo-6Si-5B-1Zr-La₂O₃ alloy at 1093 °C was comparatively investigated with other PM processed alloys, consisting of a Moₓ₋ₓ-Mo₅Si-Mo₅SiB₂ three-phase microstructure and continuous Moₙ₈ matrix phase. The corresponding Norton-plot is illustrated in Figure 3 at a temperature of 1093 °C, as a typical service temperature in high pressure turbines. For reasons of comparison previously analyzed creep data are included.

![Figure 3. Double-logarithmic plot of the creep rate vs. constant stress at 1093°C for Mo-6Si-5B-1Zr-La₂O₃ compared with other Mo-Si-B alloys.](image)

For the reference alloy Mo-6Si-5B there is only one data point available, which at least allows the assumption, that the creep performance in case of Mo-6Si-5B-1Zr-La₂O₃ may be slightly improved by the effects of alloying additions Zr and La₂O₃. In case of alloy Mo-6Si-6B-1Zr-La₂O₃ this might be explained by the mutual impact of strengthening particles which are thermally stable and reduce the creep deformation by providing obstacles to dislocation movement at high temperatures. On the other hand, the Mo-6Si-5B benefits from the larger grain size providing less creep deformation in case of grain boundary sliding.

Compared to the reference alloy Mo-9Si-8B (HIP) the Mo-6Si-5B-1Zr-La₂O₃ alloy is slightly weaker under similar creep loading. Assuming power law creep, the stress exponent is expressed as the slope $n = \Delta \log \dot{\varepsilon} / \Delta \log \sigma$ of straight lines in Figure 3. The stress exponent for Mo-6Si-5B-1Zr-La₂O₃ was found to be 2.2 and 1.9 for Mo-9Si-8B, which indicates grain boundary sliding and dislocation climb-controlled creep, which can be rationalized by the fine-grained microstructure of this type of PM alloys.

Accordingly, the creep resistance may be improved by a grain growth heat treatment [27]. In comparison, the alloy Mo-9Si-8B-1Zr, which yields a stress exponent of 3.9, shows a faster weakening especially above 150 MPa. The reasons of more significant weakening of Mo-9Si-8B and Mo-9Si-8B-1Zr at higher stresses are not clarified, yet.

At temperatures lower than 1100 °C creep Mo-Si-B samples typically show dislocation activities only in the Moₙ₈ phase, which has the lowest creep resistance in this multi-phase system [28]. Since the amount of Moₙ₈ is comparably higher (74 vol.%) than in Mo-9Si-8B (~ 50 vol.%) and Mo-9Si-8B-1Zr the creep response is mainly driven by the plastic deformation of the Moₙ₈ matrix. Considering those conditions, the creep response of the Zr-La₂O₃-modified alloy is comprehensible.
4 Summary and Conclusions
The present investigations showed how small additions of Zr and La$_2$O$_3$ can affect the room and high temperature properties of PM Mo-Si-B alloys. Finally, the following conclusions can be drawn:

1. The addition of 1 at.% Zr and 0.5 wt.% La$_2$O$_3$ to a Mo-6Si-5B alloy leads to a grain refinement of about 56%. Instead of SiO$_2$ particles, ZrO$_2$ formed, due to the getter effect on the detrimental oxygen. The La$_2$O$_3$ particles are finely dispersed within the microstructure.

2. The fracture toughness could be highly improved up to 18.8 MPam$^{1/2}$ due to the high amount (74 vol.%) of Mo$_{ss}$ matrix phase, but also caused by the grain refinement as well as grain boundary strengthening due to ZrO$_2$ and La$_2$O$_3$ particles.

3. The creep response of Mo-6Si-5B-1Zr-La$_2$O$_3$ can be well explained in comparison with other PM Mo-Si-B alloys. The Zr- and La$_2$O$_3$-modified alloy shows comparable creep exponents, indicating grain boundary sliding and dislocation climb-controlled creep. Since the amount of Mo$_{ss}$ is higher than in other PM Mo-Si-B alloys used for comparison, the creep response is mainly driven by the plastic deformation of the Mo$_{ss}$ matrix.

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