Influence of processing on the microstructure and mechanical behaviour of Mo-Si-B alloys

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Abstract. Mo-Si-B materials consisting of a Mo(Si) solid solution and the intermetallic phases Mo3Si and Mo5SiB2 (T2) were prepared by mechanical alloying (MA) as the crucial step of a powdermetallurgical process. After consolidation via an industrial processing route (cold isostatic pressing, sintering, hot isostatic pressing) the resulting microstructures of Mo-Si-B alloys up to 45% of intermetallic phases reveal a continuous $\alpha$-Mo matrix with embedded, homogeneously distributed intermetallic particles. Clearly, increasing the amount of Mo solid solution reduces the BDTT (demonstrated by three point bending tests between room temperature and 1200°C), however, values below 900°C could not be obtained due to grain boundary embrittlement caused by Si segregation. Alloying with Zr was proven by Auger analysis in Mo-Si solid solutions to reduce this segregation. Therefore, in a second trial Zr as a (micro-) alloying element was added. The influence of microalloying on ductility and strength is comparatively discussed with reference compositions Mo-6Si-5B and Mo-9Si-8B.

1. Introduction
Since three-phase Mo-Si-B alloys (pioneered by Berczik [1]) combine the excellent high temperature strength of Mo-base alloys and the beneficial oxidation resistance of intermetallic silicide phases as a provider for Si and B necessary for forming a dense coating consisting of SiO2(B) glass [2], they are considered as candidates for high temperature application in air. It is widely accepted that the ideal microstructure of these alloys is composed of a continuous $\alpha$-Mo matrix with embedded intermetallic particles [3-7]. A powdermetallurgical (PM) process based on mechanical alloying (MA) as the crucial step may be used to fabricate three-phase Mo-Si-B alloys with this microstructure. In previous work [8] it was demonstrated that while Si is one of the most effective solid solution strengtheners for Mo [9], it also strongly promotes the tendency towards brittle intergranular failure. Amongst other possible elements that potentially ductilize Mo [10], Zr has been shown to improve the fracture toughness of Mo-12Si-8.5B [5]. Miller and Bryhan [11] have demonstrated by atom probe tomography that small amounts of Zr, C and B substitute detrimental oxygen at the grain boundaries.
of a welded Mo-base alloy. Therefore, in our recent work [12] we studied the mechanical behaviour of mechanically alloyed Mo-1.5Si and Mo-1.5Si-1Zr as compared to Mo-0.3Si and Mo-1.5Si processed by an industrial PM route (without MA). We have shown that the brittle behaviour of Mo(Si) at room temperature is, at least in part, caused by the reduction of the cohesive grain boundary strength due to segregated Si. As an important outcome Auger analysis showed that additions of Zr dramatically reduce the segregation of Si at the grain boundaries [12]. Furthermore, Zr is responsible not only for the reduction of the grain size of (single phase) Mo-Si solid solutions, additionally it improves the strength level from 500 MPa to about 2 GPa and leads to limited plastic deformation in RT bend tests. Therefore, in this paper we investigate the effect of Zr on the mechanical properties of three phase Mo-Si-B alloys between RT and 1200°C.

2. Experimental
Elemental powder mixtures of Mo, Si and B of 99.95, 99.9 and 98% purity respectively, were used to produce different ternary Mo-Si-B compositions. Mechanical alloying (MA, high energy milling) was carried out under protective argon atmosphere for 20 hours in a planetary ball mill (Retsch® PM 400) with a rotational speed of 200 rpm and a powder to ball weight ratio of 1:13. After milling, the powders were cold isostatically pressed at 200 MPa and sintered under hydrogen atmosphere at 1600°C to reduce the impurity content (mainly oxygen). As a final step the sintered bars were further consolidated by hot isostatic pressing (HIP) at 1500°C and 200 MPa. The microstructures of powder samples were characterized by X-ray diffraction (XRD) with CuKα radiation. Lattice parameters of α-Mo were calculated on the basis of seven peaks using the Cohen Method [13]. To determine the domain size of the milled powders, the program “breadth” [14] based on the Fourier method was used. The microstructures of consolidated samples were characterized by scanning electron microscopy (FEI ESEM XL30 FEG equipped with EDX). Mechanical properties were assessed by three-point bending tests using rectangular samples with a cross section of about 3.8 x 3 mm² which were prepared from HIPed bars by electro-discharge machining, turning and grinding. All tests were carried out using a Zwick electromechanical testing device equipped with a Maytec furnace at a crosshead speed of 0.01 mm/min. Above 500°C the tests were performed under protective argon atmosphere.

3. Results and Discussion
In Table 1 the powder parameters during mechanical alloying are summarized for Mo-9Si-8B. The domain size decreases right from the beginning of MA followed by the decrease of the lattice parameter after 10 h of milling. Since the atomic radius of Si is significantly smaller than that of Mo, it is obvious that substitution of Mo by different proportions of Si atoms leads to the observed decrease of the lattice parameter with increasing Si solution. While MA of Mo-4Si-2B (not shown here, see [6]) leads to a nearly constant lattice parameter after milling times longer than 30 hours, the lattice parameter of powder mixtures with higher Si and B content still decreases up to larger milling times indicating further solution of Si. The formation of a solid solution also becomes apparent in the increasing hardness values during milling.

Table 1. Powder parameters of Mo-9Si-8B in dependence on the milling time.

| Alloy      | Mo-9Si-8B |
|-----------|-----------|
| Milling time [h] | 5 | 10 | 20 | 30 | 50 | 70 | 100 |
| Lattice constant of α-Mo [Å] | 3.1471 | 3.1466 | 3.1419 | 3.1372 | 3.1276 | 3.1227 | 3.1144 |
| Domain size of α-Mo [Å] | 150 | 64 | - | 93 | 31 | 21 | 12 |
| Microhardness (HV 0.01/5) | 1089 | 1176 | 1177 | - | 1215 | 1284 | 1334 |
Microstructures of the consolidated Mo-Si-B samples. The α-Mo matrix appears as the brightest phase and the slightly darker grey and the dark grey appearing phases are Mo$_3$Si and Mo$_5$SiB$_2$.

The consolidation as described in the experimental section leads to the formation of an optimal microstructure consisting of a continuous α-Mo matrix (light-grey) and embedded intermetallic particles (dark-grey) for both, the Mo-6Si-5B and Mo-9Si-8B composition, respectively. This is shown in the 2D SEM micrographs in figure 1. In contrast the alloys Mo-10Si-10B and Mo-13Si-12B show a reversed microstructure, namely a continuous intermetallic matrix with islands of α-Mo. These findings have been recently confirmed by 3D SEM FIB tomography [15]. Generally, the materials processed through MA show a very fine microstructure with the average grain sizes of all phases as determined by quantitative stereology to lie between 1 and 1.5 µm [6].

**Figure 1.** Microstructures of the consolidated Mo-Si-B samples. The α-Mo matrix appears as the brightest phase and the slightly darker grey and the dark grey appearing phases are Mo$_3$Si and Mo$_5$SiB$_2$.

**Figure 2.** Stress-strain-curves (outer fibre) of Mo-Si-B alloys at RT and 954°C.

Stress-strain (calculated for the outer tensile fibre) curves for the Mo-Si-B base alloys and two alloys with additions of 1% Zr at RT and 954°C are compared in figure 2. All tested alloys behave brittle at RT, though Zr apparently causes an increased strength level of up to 1600 MPa. This is approximately a factor of 2 larger than the values reported in [1] for the same base composition. Furthermore, Zr leads to limited plastic deformation at temperatures as low as 800°C (light blue curve in figure 3), whereas the base alloys remain still brittle up to about 950°C. Consequently, the brittle-to-ductile transition temperature (BDTT) of alloys with a continuous α-Mo matrix could be reduced by about 150°C and by more than 250°C as compared with alloys possessing an intermetallic matrix (orange...
and green in figure 3). Future work will be directed towards varying the necessary Zr concentration or finding other potentially ductilizing elements to fully exploit the effect on reducing of the BDTT.

Figure 3. Outer fibre tensile fracture strain of mechanically alloyed Mo-Si-B alloys versus test temperature showing the decrease of BDTT for alloys with continuous α-Mo matrix and the effect of Zr microalloying which decreases the BDTT of these alloys even further. Note that the tests were terminated after reaching 8% plastic strain even if fracture did not occur.

4. Conclusions
Mechanical alloying offers the opportunity to prepare three-phase Mo-Si-B alloys that possess a continuous α-Mo matrix in which uniformly distributed intermetallic particles are embedded. The BDTT decreases by about 150 K when a continuous α-Mo matrix is established instead of an intermetallic matrix. A further improvement of the ductility of Mo-Si-B alloys with continuous α-Mo matrix is reached by the addition of Zr, which in Mo-Si alloys has already been identified as reducing the segregation of Si to the grain boundaries, thus enhancing their cohesive strength dramatically [12].

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