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# Grain boundary segregation engineering in as-sintered molybdenum for improved ductility

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ABSTRACT

The characteristics of grain boundaries and their influence on the mechanical properties have become key issues in recent research on structural materials. Especially in molybdenum, grain boundary segregation plays a significant role regarding ductility and strength. In this study as-sintered conditions of technically pure as well as boron and carbon doped molybdenum were mechanically characterized by bending tests and correspondingly analyzed by atom probe tomography to understand the differences in mechanical behavior after alloying. Strategies for improving the ductility of molybdenum are discussed with special focus on grain boundary segregation.



Molybdenum is a refractory metal which is perfectly suited for many high-performance structural and functional applications. However, a ductile-to-brittle transition temperature (DBTT) close to room temperature (RT), as well as increased embrittlement of the recrystallized state complicates the production and the use of molybdenum as a structural material [1].

In general, molybdenum is known to have the disadvantage of intrinsically weak grain boundaries [2–6]. Particularly, random high-angle grain boundaries have a low resistance against crack propagation which results in failure dominated by intergranular fracture [5, 7, 8]. Nevertheless, it is also known that extrinsic effects, like solute segregation at grain boundaries, may contribute significantly to the strength and ductility of molybdenum [1, 9–14]. Latest atom probe studies have shown that oxygen, nitrogen, carbon and phosphorus are typical grain boundary segregation elements in powder-metallurgical (PM) technically pure molybdenum [15–18]. Especially oxygen is known to segregate to grain boundaries in several molybdenum alloys [1, 12, 19, 20] and to evoke intergranular fracture by decreasing the grain boundary strength [1, 12, 21–24]. First-principle calculations confirm these detrimental effects [25] and recommend the suppression of oxygen enrichments in molybdenum. Additionally, the presence of nitrogen and phosphorus at grain boundaries is suggested to have negative consequences on the cohesion of grain boundaries, promoting intergranular fracture [25–28]. In order to overcome the problem of intergranular embrittlement and to lower the DBTT of molybdenum, the local grain boundary chemistry can be modified by the introduction of certain elements which strengthen the grain boundaries. From literature it is well known that especially carbon and boron have a strengthening effect on grain boundaries in molybdenum, causing a decrease of the DBTT and promoting transgranular fracture [11, 14, 22, 23, 29–35]. Therefore, in this work pure molybdenum (Pure Mo) is compared to carbon (MoC) and boron (MoB) doped molybdenum in as-sintered conditions without any deformation or additional heat treatment history regarding the influences of segregation mechanisms on the mechanical behavior.

Experimentally, molybdenum rods (diameter 30 mm) were produced by the typical PM-route of powder mixing, cold-isostatic pressing between 150 and 250 MPa and sintering under protective hydrogen atmosphere above 2073 K [36]. To exclude effects of any deformation and heat treatment history, the as-sintered condition was chosen for this investigation. Therefore, changes in the mechanical properties can be directly correlated to segregation effects without any influences of the microstructural evolution. The chemistry of the main alloying and impurity elements of the three sample materials is given in Table 1.

For the microstructural characterization electron-backscatter diffraction (EBSD) analyses were performed in a FEI Versa 3D DualBeam microscope in analytical mode equipped with an EDAX Hikari XP camera. The metallographic preparation for all microstructural characterizations was performed by mechanical grinding and polishing followed by an electrolytic polishing with a 12.5 vol% $H_2SO_4$ solution in ethanol [37,

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**Table 1**
Chemical composition of the doping and alloying elements and main impurities in μg/g of the three investigated molybdenum samples (Pure Mo, MoC and MoB).

| | B[a] | C[b] | O[c] | N[c] | P[a] | S[b] |
|---|---|---|---|---|---|---|
| Pure Mo | 2 | 3 | 9 | 4 | 3 | 0 |
| MoC | 2 | 55 | <5 | <5 | 2 | <5 |
| MoB | 63 | 7 | 5 | 3 | 3 | 1 |

[a] Inductively coupled plasma-atomic emission spectrometry.
[b] Combustion analysis.
[c] Carrier-gas analysis.

38]. For the EBSD analyses an acceleration voltage of 20 kV, a 6 × 6 binning, a working distance of 10 mm and a current of 11 nA with a step size of 1 μm were used. The obtained data was evaluated with the EDAX OIM Analysis 7 software. The mechanical behavior is exemplified by three-point-bending experiments on samples with 6 × 6 $mm^2$ cross-section and 30 mm length on a Zwick 1478 testing machine. The samples were analyzed in the as-sintered condition with ground specimen surfaces between −60 °C and 180 °C after a stress-relieve annealing at 760 °C/2 h in dry hydrogen atmosphere (according to ASTM B386 and ASTM B387). The specimens were heated in a Mytec heating chamber under air atmosphere and cooled inside a vessel filled with an alcohol-liquid-nitrogen mixture. For all experiments, testing was started 10 min after reaching the desired testing temperature and the temperature was measured directly on the sample with a Ni-CrNi-thermocouple with an accuracy of at least ±5 K. The gauge distance of the bending aperture was 20 mm, the radius of the supporting bolts 1.5 mm and the test velocity 10 mm/min. The fracture surfaces as well as the DBTT were evaluated of the tested specimens. Therefore, the DBTT was defined as temperature between the temperature of brittle fracture and the temperature of ductile bending (no fracture).

In Fig. 1 the microstructure and the fracture surfaces of the samples tested at RT are illustrated. All three samples show a typical sintered microstructure with comparable grain sizes between 31 and 33 μm with a quite large standard deviation indicating the broad size distribution of the grains in all three states (Fig. 1a–c). The majority of insufficiently indexed points are sinter pores, which are usually present in the as-sintered material condition and have been enlarged by electropolishing. The corresponding fracture surfaces from the mechanical bending experiments reveal that Pure Mo (see Fig. 1d) exhibits primarily intergranular fracture, whereas, the fracture surfaces of alloy MoC (Fig. 1e) and MoB (Fig. 1f) are dominated by transgranular fracture. In Fig. 1d intergranular fracture can be assumed, where contours of former grains are visible on the fracture surface (see marked area). Areas with transgranular fracture are characterized by a rougher and more unregularly shaped appearance (see Fig. 1e and f, marked area). To get an overview of the change in mechanical behavior after carbon and boron addition the DBTT in °C is listed in Fig. 1. It is obvious that Pure Mo exhibits the highest DBTT of 135 °C followed by the carbon rich alloy (60 °C). For alloy MoB the lowest DBTT was measured (0 °C).

However, to understand the change of the DBTT and the corresponding fracture mode, a thorough characterization of the grain boundary chemistry has to be done. Thus, atom probe tomography (APT) was used to obtain atomic-scale analyses of the high-angle grain boundary chemistry for all three molybdenum conditions (Pure Mo, MoC, MoB). The atom probe specimens were prepared with the new technique of correlative transmission Kikuchi diffraction (TKD) [15, 18]. On the one hand this method was applied on pre-electro polished tips as described in [15]. On the other hand, specific grain boundaries were selected by using EBSD, lifted out and finally prepared by TKD [17]. The APT measurements were conducted in a Cameca LEAP 3000 X HR instrument in the laser mode with 0.6 nJ laser energy (525 nm laser with ~10 μm spot size), 250 kHz pulse repetition rate at a set temperature of 60 K, and a detection rate of 0.005 atoms per pulse. The IVAS 3.6.8 software was used for the reconstruction of the measured data.

In Fig. 2 the atomic grain boundary chemistry of the three different molybdenum samples is shown by representative three-dimensional reconstruction of the APT data sets. At least two grain boundaries were prepared of each sample material for the characterization in the atom probe. One measurement was successful for Pure Mo and MoC, whereas four grain boundaries could be analyzed in MoB. In order to aid clarity, the molybdenum atoms are blanked in the images and only the segregating elements are displayed. At the grain boundary of Pure Mo (Fig. 2a, misorientation of 49°) small amounts of oxygen, phosphorus and nitrogen can be found. The grain boundary of alloy MoC (Fig. 2b, misorientation of 44°) additionally exhibits high enrichments of carbon

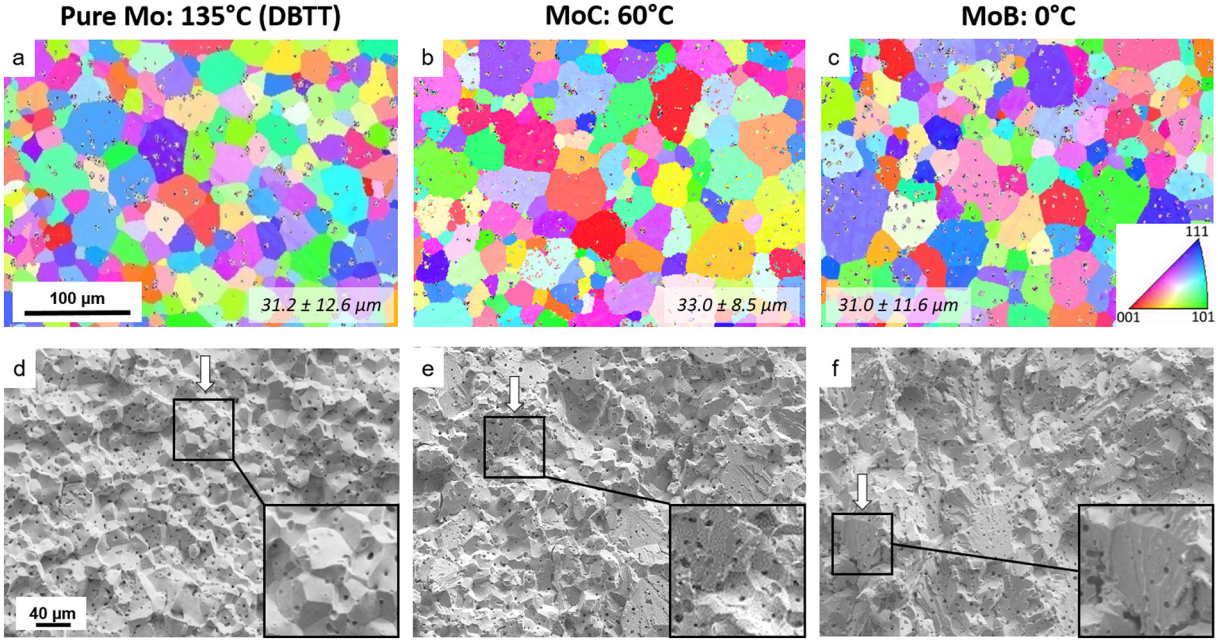


**Fig. 1.** The microstructure analyzed by EBSD is shown for Pure Mo (a), MoC (b), and MoB (c). The majority of mis-indexed points are sinter pores, which are also visible in the SEM images in d-f. In (d-f) the corresponding fracture surfaces after three-point bending experiments around RT are illustrated. Pure Mo (d) exhibits intergranular fracture, whereas MoC (e) and MoB (f) show mainly transgranular fracture. The DBTT decreases from 135 °C (Pure Mo) to 60 °C (MoC) to 0 °C (MoB).