Recent advances in additive manufacturing of Mo-Si-B alloys – A status report on the cooperative project LextrA -

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Abstract. Mo-Si-B alloys are potential materials for ultra-high temperature applications, e.g. as turbine blades. Due to their excellent mechanical properties they are subject to basic research for about 20 years. The next step towards industrial application of this type of alloys is to use the current knowledge on microstructure-properties relationships and combine this with innovative laser additive manufacturing (AM). This way of processing is very challenging since the melting point of Mo-Si-B materials is > 2000 °C and the brittle-to-ductile transition temperature is typically about 900 °C. The authors demonstrate that gas atomized Mo-Si-B powders of three different compositions could be successfully processed by different AM processes, namely Direct Energy Deposition (DED) and Laser Powder Bed Fusion (LPBF). It is verified that the mechanical and oxidation properties provided by the AM materials are comparable and competitive to similar alloy compositions from conventional processes.

1 Introduction

The demand for novel materials for structural high temperature applications results in extensive research on high strength metallic and intermetallic materials. Aiming in resource-saving, sustainable and cost-efficient industrial processes the development of new materials must be combined with innovative processing methods. For improving the efficiency of gas or airplane turbines, new materials beyond the capability of Ni-based superalloys are under consideration [1–3]. Besides others, multi-phase Mo-Si-B alloys are seen as potential substitutes, as they provide improved creep resistance, good fracture
toughness and high thermal resistance. Simulations and comparative experimental assessments against Ni-base superalloys already demonstrated the outstanding performance of Mo-Si-B alloys [4–6].

In the past two decades basic research was dedicated to basic understanding of microstructural evolution, phase equilibria, different options of processing and application-related properties as fracture toughness, creep response and oxidation behavior [7–10]. In terms of bulk processing two general approaches were followed in the past, i.e. processes that are based on phase transformations from a molten phase (classical ingot metallurgy, directional solidification) or processes based on diffusion and/or phase transformation mechanisms in the solid state (powder metallurgical processes). The classical melting processes are very energy-intensive and costly due to ultra-high melting points of Mo-based materials up to 2600°C, and does not allow a high degree of freedom in terms of tailoring properties due to inhomogeneous microstructural evolution of the individual phases. An exception are eutectic or near-eutectic alloys having a melting point < 2100 °C, which show very fine network-like microstructures. Such eutectic microstructures can be grown directionally to provide anisotropic materials properties [11–13]. The more established processes are powder metallurgical (PM) processes that avoid phase formation from the melt and therefore, allows the formation of very fine-grained and homogenous microstructures with typical isotropic properties. Furthermore, by PM techniques different additional elements or compounds can be incorporated in the alloys to modify their properties in a wide range [7]. However, using the above-mentioned processing methods extensive mechanical finishing will be necessary to produce complex parts like turbine blades with cooling structures. This is challenging due to the extremely hard silicide phases in Mo-Si-B alloys.

In our present approach we use the basic knowledge on the microstructural evolution of Mo-Si-B alloys and combine this with new processing methods aiming in manufacturing of net-shaped materials (Fig. 1). In the framework of the project LextrA (full title in German: Laserbasierte additive Fertigung von Bauteilen für extreme Anforderungen aus innovativen intermetallischen Werkstoffen) a consortium of industrial partners (Siemens AG, Nanoval, Kochanek Entwicklungsgesellschaft, IfKorr) and research institutes (Fraunhofer ILT Aachen, Otto-von-Guericke University Magdeburg) focuses on the industrial application of additive manufacturing (AM) of new materials, i.e. Mo-Si-B, V-Si-B and Fe-Al alloys. These groups of intermetallic materials were identified as potential candidates for turbine blade materials in different stages of gas turbines.

To date there is just a small number of publications on additive manufacturing of Mo-based alloys worldwide, because this field of research is very challenging from the technical and metallurgical point of view [15–17]. The present manuscript will concentrate on the advances that were achieved within the project LextrA with respect to DED (Direct Energy Deposition) and LPBF (Laser Powder Bed Fusion) processing of Mo-Si-B materials. Experimental findings on AM of other high temperature materials, namely multi-phase V-Si-B alloys, are published recently elsewhere [18].
2 Materials and Methods

The alloys Mo-9Si-8B, Mo-13.5Si-7.5B and Mo-16.5Si-7.5B (in at.%) were chosen for this study. Alloy Mo-9Si-8B is a reference alloy for the Mo-rich Mo-Si-B materials, for which a large database is available in literature [6,7,10,19]. Both alloys with higher silicon and boron concentrations are close to the eutectic point and provide therefore, a lower melting point as compared to the reference alloy, which could make manufacturing more energy-efficient and at least provides a very defined microstructure [11,20]. The powders for the AM processes were processed by gas atomization (GA). The solid raw materials (Mo > 99.95%, Si > 99.6% and B > 99.4% purity) were molten and superheated in a crucible (inductive heating system) and subsequently atomized into alloyed powders. More details on this process are given in [21]. The powders were investigated by SEM in combination with EDS to analyze the morphology, the chemical homogeneity and potential agglomeration or satellite formation. Microscopic images of the three Mo-Si-B powders are presented in Figure 2, which show mainly spherical morphology that is mandatory for a good flowability during the AM process.

![Figure 2. Micrographs of gas atomized powders of alloys (a) Mo-13.5Si-7.5B for processing via DED as well as (b) Mo-9Si-8B and (c) Mo-16.5Si-7.5B for AM via LPBF.](image)

After GA the powders were sized to fractions of +45/−90 μm for the DED and +15/−45 μm for the LPBF process. It is known from refractory powders that they absorb impurities from the environment over time depending on storage [22], especially embrittling oxygen. Due to these reasons, the powders were heat treated before LPBF processing to “clean” the surfaces and therefore, avoid crack formation in the AM builds. A specific technical requirement for successful processing of crack-free Mo-Si-B samples is the need of high pre-heating temperatures, i.e. approx. 700 °C for the DED process and up to 1200 °C in the substrate for LPBF process. More details on the LPBF are described more specifically in [23,24], the description of the DED process is provided in [18,21,25].

The microstructures of the AM builds were investigated in terms of their microstructural evolution by SEM and EBSD methods. Phase fractions were determined and compared to literature data of existing phase diagrams and other Mo-Si-B alloys. For analyzing the porosity, image analysis was performed by using both the software Stream Motion (Olympus) and ImageJ, working on the principle of separating different grey values.

The high temperature mechanical properties were determined by means of compressive creep tests. Parallelepiped-shaped specimen were electro-discharge machined from the AM builds with dimensions of 2 mm x 2 mm x 3.5 mm. All creep tests were carried out under constant true stress or constant strain using a Zwick electromechanical testing device equipped with a Maytec furnace at temperatures at 1093 °C, which involved continuous monitoring of creep strain and stress throughout the test.

Cyclic oxidation tests were performed at 800 °C, 1100 °C and 1300 °C to get an idea on the oxidation response in the so-called pesting regime [9] and at potential application temperatures, respectively. Therefore, samples were put into a hot furnace under atmospheric conditions, exposed for a certain period of time and then removed. Afterwards, the surface of the materials was recorded by optical microscopy and the weight change was monitored by weighing the samples after each removal from the furnace treatment.
3 Results and Discussion

This paragraph provides an overview on the microstructures of AM Mo-Si-B builds evolving from the DED and LPBF processes as well as selected results on the mechanical behavior of AM materials in comparison to data from differently processed materials. Additional materials properties determined at room temperature and elevated temperatures can be found in [21,24,25]. Furthermore, first insights into the oxidation response of AM Mo-Si-B materials will be given.

3.1 Additively manufactured compacts and microstructures

Typical macroscopic cross sections of AM alloys, i.e. LPBF Mo-16.5Si-7.5B, DED Mo-13.5Si-7.5B, and DED Mo-9Si-8B as well as a hollow AM structure are presented in Figure 3. Samples with different geometries show the processability of this type of material. In general, typical defects in such high melting multi-phase intermetallic materials are cracks or ablation in consequence of internal stresses as well as porosity. In another study internal microcracks were observed which are assumed to reduce the hardness as compared to as-cast alloys and might also be responsible for premature failure of AM alloys [17]. Due to pre-heating of substrates in LPBF process [24] and using a movable induction coil for DED processing [25] cracks could be avoided in our experiments (Fig. 3). However, there is residual porosity, which in case of LPBF specimen is typically <1 %, while DED samples have a porosity of about 2 %.

![Figure 3. Macroscopic cross sections of (A) LPBF build of alloy Mo-16.5Si-7.5B and DED builds of (B) alloy Mo-13.5Si-7.5B and (C) alloy Mo-9Si-8B as well as (D) hollow structure of Mo-9Si-8B produced by DED.](image)

The microstructure of the builds was investigated by SEM in combination with EBSD, as exemplarily shown in Figure 4 for three different AM alloys. Distinct zones resulting from the layer-wise laser processing were also observed and described in [21]. However, the overall microstructure evolution in AM processes seems to be quite familiar, since it has a similar morphology as compared to microstructures as solidified from other melting processes. In case of alloy Mo-9Si-8B, which is located in the primary solidification area of Mo solid solution (Mo₉ₓ), large dendrites of this phase (red in Fig. 4) are formed, before the residual melt solidifies in eutectic structures, finally reaching the ternary eutectic Mo₉ₓ-Mo₅Si-Mo₅SiB₂. Interestingly, the observed microstructural evolution is in good agreement with the sequence of solidification analyzed by arc-melting experiments as well as the predictions of phase equilibria from the Mo-rich corner of the ternary Mo-Si-B phase diagram [26,27]. However, our results are in contrast to Makineni et al. [16], who found the constituents Mo₉ₓ, Mo₅SiB₂ and Mo₅Si₁ in ball-milled and laser-melted alloy Mo-8.5Si-5.6B, of which the composition is very close to alloy Mo-9Si-8B. This difference is assumed to be due to rapid quenching and accompanying non-equilibrium conditions in the process of Makineni [16].

Alloys with higher Si and B concentrations are located closer to the binary eutectic valleys and/or to the ternary eutectic point as described recently by Hasemann et al. [26]. Consequently, the content of the Mo₉ₓ primary phase in Mo-13.5Si-7.5B is less than in Mo-9Si-8B (see Fig. 4). Furthermore, the alloy Mo-16.5Si-7.5B entirely provides a ternary eutectic microstructure consisting of the phases Mo₉ₓ (red), Mo₅Si (blue) and Mo₅SiB₂ (yellow), which again is in very good agreement with observations from other melting processes [26,28]. This gives evidence that the additive manufacturing processes used in
this study result in (near-) equilibrium microstructures. It is well-known that phase transformations are not existing within the three-phase region of Mo₉₅Mo₆₅Si-Mo₅₅SiB₂ up to temperatures of at least 1800 °C [28]. Therefore, it can be assumed that significant and sudden modifications of the properties due to phase transformations will not occur during static or cyclic thermal loadings at potential application temperatures of turbine blades.

The present results show that Mo-rich multi-phase Mo-Si-B alloys with ultra-high melting points between ~ 2050 °C < T < 2400 °C can be processed not only with near-equilibrium microstructures but also free of cracks by using pre-alloyed gas atomized powders and the tailored additive manufacturing techniques DED and LPBF.

Figure 4. Microstructures of AM Mo-Si-B alloys with primary Mo solidification (Mo-9Si-8B and Mo-13.5Si-7.5B) as well as near eutectic (Mo-16.5Si-7.5B) in context of a recently published liquidus projection (reproduction from [26] provided by G. Hasemann).

3.2 Mechanical properties in comparison to literature data
The mechanical properties of the alloys were analyzed from room temperature up to high potential application temperatures. In previous studies on PM Mo-Si-B materials it was found that alloys with higher Mo₉₅ concentrations tend to provide improved mechanical characteristics at ambient temperatures, e.g. a higher fracture toughness and reduced brittle-to-ductile-transition temperatures (BDTT), while alloys with higher silicide concentrations have an improved creep resistance and reduced oxidation rates [7].

Hardness measurements of DED materials as presented in [21] as well as for LPBF samples [24] show a very good agreement with the values for Mo-Si-B alloys achieved by other processes [7,29]. It is important to note, that the macrohardness of the alloy is typically in between the hardness of the Mo₉₅ phase (2…10 GPa, depending on the concentration of dissolved elements and the grain size) and the hardness of the eutectic regions (16…20 GPa). These results indicate that the strength of AM alloys at room temperature could also be competitive compared with conventionally processed Mo-Si-B materials, but was not proven by tensile tests, yet. However, first bending tests provide new insights into the temperature-dependent flexural stress-strain data and, therefore, the BDTT. These results, which will be presented in detail in [24], show that there is even an improvement of the ductility of the AM material at 950 °C in comparison with PM Mo-Si-B alloys.
A very important issue in terms of application in a gas turbine is the creep resistance of Mo-Si-B alloys. In our earlier work we found out that the creep resistance is improved against the state-of-the-art turbine blade materials nickel-based superalloys at their typical application temperatures around 1100 °C. This advantage becomes even more pronounced at higher temperatures of 1200 °C, which could be a potential application temperature of turbines using new high-temperature resistant Mo-Si-B materials [6,12].

For the first time, the time-dependent deformability of AM alloys at constant applied stresses was investigated within the project LextrA by the same experimental procedure as used for other Mo-Si-B alloys in previous studies. This enables a direct comparison of AM Mo-Si-B alloys with powder metallurgical (PM) processed as well as arc-melted (ARC) and zone melted (ZM) alloys [12,30]. The results are presented as a double-logarithmic representation of the minimum creep rate vs. applied stress (so-called Norton plot) in Figure 5. All Mo-Si-B alloys show a significantly improved creep resistance compared to pure Mo, which is due to the much more creep resistant silicide phases \( \text{Mo}_3\text{Si} \) and \( \text{Mo}_5\text{SiB}_2 \) vs. bcc Mo or the Mo\textsubscript{ss} phase. Furthermore, there is a strong divergence between the creep strength of alloys Mo-9Si-8B (with ~ 50 % Mo\textsubscript{ss}) and the near-eutectic alloys with ~ 20 – 30 % Mo\textsubscript{ss}. The reasons are seen mainly in the Mo\textsubscript{ss} volume fraction. Additionally, the distribution of the phases (network-like or interpenetrating structure of PM alloys vs. typical cast microstructures of ARC and AM alloys) and the size-scale of the constituents play a role to understand the creep response of the alloys. Due to the ultra-fine grained structure of eutectic AM alloys, the lower creep resistance of AM alloys against ARC alloy could be rationalized. TEM analyzes should help to understand the creep mechanism of AM alloys and are subject of ongoing research. However, from other research on fine-grained Mo-Si-B materials it is already known that heat treatments targeted in grain growth will improve the creep resistance. This must be proven for the novel AM materials.

![Figure 5. Norton plot of differently processed Mo-Si-B alloys at a potential application temperature of 1093 °C.](image.png)

![Figure 6. DED Mo-9Si-8B after oxidation for 100 h at 1300 °C.](image.png)

### 3.3 Oxidation response

The interaction of Mo-Si-B alloys with the environment at different temperatures plays a key role for potential applications as turbine blade materials. It is well-known that Mo-Si-B alloys suffer from the so-called pesting phenomenon, which is accompanied with catastrophic mass loss at intermediate temperatures due to MoO\(_3\) formation and evaporation [9]. Depending on the microstructures, especially on the fraction, size scale and distribution of the Mo\textsubscript{ss} phase, the quantity of mass loss will be affected. At higher temperatures, e.g. 1100 °C, the formation of a well-sticking borosilicate glass layer may protect the surface from further oxidation if the Mo\textsubscript{ss} concentration in the alloy is not higher than 50% and the phases size is in the lower \(\mu\text{m}\)-range [7,9].
In this work the AM materials were exposed to air for certain periods and the mass change was determined in correlation to the surface area of samples. The AM materials show a similar behavior as compared to other Mo-Si-B alloys in dependence on the microstructural features as addressed before. Therefore, it is not surprising that the highest mass loss of the AM Mo-Si-B samples is observed after treatment at 800 °C as it is a known mechanism [9]. In contrast, there is just a small mass loss observed at 1100 °C and 1300 °C and the shape of samples was preserved after oxidation treatment due to the self-protection mechanism by protective glass formation at the surface. This behavior is, of course, dependent on the alloy composition and other parameters. An example of the macroscopic morphology of the DED Mo-9Si-8B alloy after oxidation treatment at 1300 °C for 100 h is provided in Figure 6. More details on the oxidation response at different temperatures and data on specific mass change of AM Mo-16.5Si-7.5B material will be presented elsewhere [31].

However, there are some potential approaches to protect Mo-Si-B alloys from environmental degradation by different coating strategies, like sputtering techniques, pack cementation and dip-coating methods [32–34]. These strategies typically follow the target to protect Mo-based alloys with layers of oxidation-resistant silicides, which have a similar thermal expansion coefficient as the substrate materials. Therefore, it is expected that coatings will solve the problem of oxidation sensitivity of Mo$_{53}$-rich Mo-Si-B alloys in the future.

4 Summary and Conclusions
This work shows the successful additive manufacturing of Mo-Si-B bulk materials by Laser Powder Bed Fusion (LPBF) and Direct Energy Deposition (DED). This way of processing is very challenging since the melting point of Mo-Si-B materials is > 2000 °C and the brittle-to-ductile transition temperature is typically higher than 900 °C. Three different alloys taken from the Mo-rich corner of the Mo-Si-B system were investigated: Mo-9Si-8B, Mo-13.5Si-7.5B and Mo-16.5Si-7.5B. For both AM processes size-fractioned gas atomized powders were used. An important outcome is that the bulk materials of the three alloys were processed free of cracks, but they have a residual porosity of < 1% in case of LPBF and < 2% in case of DED. It could be shown that the microstructure of all alloys correspond to the equilibrium phase fractions of Mo$_{53}$, Mo$_5$Si and Mo$_5$SiB$_2$ as expected by the phase diagram. Therefore, no additional heat treatment was necessary to achieve equilibrium microstructures.

In this study the creep resistance of LPBF and DED Mo-Si-B materials were comparatively assessed against Mo-Si-B materials from powder metallurgical, arc-melting and zone melting processes. This data shows that the high temperature mechanical properties provided by the AM materials are comparable and competitive to similar alloy compositions from conventional processes. There is an additional improvement of the creep resistance possible by grain growth annealing of the ultra-fine-grained eutectic alloys. Furthermore, the AM materials were exposed to laboratory air for certain periods of time and at different application-related temperatures. In general, the oxidation response of the AM alloys is similar to other well-known Mo-Si-B alloys. The highest mass loss was observed at 800 °C, which is well-known as the so-called pesting phenomenon. At 1100 °C as well as at 1300 °C a protective borosilicate glass layer forms at the surface of the Mo-Si-B materials, which prevents the materials from further oxidation and, therefore, avoids further mass losses.

The results of this project provide new insights into the possibilities given by additive manufacturing processes in connection with the challenging class of ultra-high melting multi-phase Mo-Si-B alloys. First evaluation of mechanical and oxidation properties show the great potential of AM Mo-Si-B materials as they have shown to be competitive to conventional processes. More detailed analyses of the mechanical behavior and the oxidation behavior of AM Mo-Si-B will be published soon [24,31].

Acknowledgements
This work was supported by the German Ministry of Education and Research BMBF (funding number: 03XP0094) within the funding program “ProMat_3D”.
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