High Temperature Oxidation of Multiphase Mo-Si-B-X Alloys

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Summary
Nowadays, even fourth generation nickel-base superalloys are approaching their fundamental limitation – the melting point. Hence, a further increase of efficiency, i.e. of jet engines, can only be realized by developing new materials for the use at temperatures beyond 1200°C. A new alloy concept using the Mo-Si-B system for ultra-high temperature applications is discussed. Those alloys have melting points around 2000°C, while retaining good mechanical properties and oxidation resistance in the desired temperature range.

A three-phase Mo-9Si-8B alloy (composition in at.%) consisting of α-Mo, Mo\textsubscript{3}Si and Mo\textsubscript{5}SiB\textsubscript{2} (T2) was produced by powder metallurgical (PM) processing route and exposed at 1700°C in laboratory atmosphere. At temperatures higher than 1000°C in laboratory air, a protective SiO\textsubscript{2}/B\textsubscript{2}O\textsubscript{3} glass layer develops on the alloy surface giving excellent oxidation resistance. However, in the temperature range between 700°C and 900°C, non-protective and highly volatile molybdenum oxides form causing the disintegration of the material (the so-called pesting phenomenon). Additions of Zr and La\textsubscript{2}O\textsubscript{3} to the Mo-Si-B alloy systems were investigated in order to improve the performance of the alloys in the pesting temperature range. The oxidation kinetics was determined by means of thermogravimetric analysis (TGA) and discontinuous oxidation experiments. Microstructural examinations were performed by means of optical and scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS). The microstructural observations were compared with the theoretical prediction of phase stability using computational thermodynamic calculations.

A significant improvement of the alloys during oxidation in the pesting temperature range was found. The rate of formation of molybdenum oxides could be drastically reduced at intermediate temperature range. At high temperatures (>1000°C), a homogeneous and protective SiO\textsubscript{2} oxide layer was formed on the alloy surface leading to a slow growing oxide scale.

1. Introduction
Using refractory metals (RM), ceramic materials or intermetallic compounds for high temperature applications has become a challenging research in the past decades while aiming for temperature environments of 1300°C and above. However, in a single component form, these materials rarely satisfy requirements such as high melting point, oxidation resistance and structural functionality because of the brittleness of ceramic materials and intermetallic compounds at low temperatures and the oxidation problems as well as poor creep resistance of refractory metals at high temperatures.

At elevated temperatures, alloy phases containing Al or Si are attractive for developing thermodynamically stable Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} (silica) oxide films. At 1300°C, SiO\textsubscript{2} films are preferred since their parabolic rate constant is lower than the one of Al\textsubscript{2}O\textsubscript{3} films [1]. For static high temperature applications, e.g. furnace heating
elements, MoSi₂, which is having excellent oxidation resistance, has been in use for a long time. Nevertheless, at high temperatures the creep strength is insufficient and at low temperatures it suffers from brittle behaviour [2]. Mo-based alloys in the form of intermetallic Mo-Si-B alloys seem to be favourable due to their promising mechanical properties. At room temperature Mo has a low thermal expansion coefficient along with a high thermal conductivity.

Intermetallic phases are used for high temperature properties and a ductile Mo phase for fracture toughness. Still the key issue continues to be the oxidation resistance. Figure 1 shows the Mo-rich corner of the Mo-Si-B ternary phase diagram at 1600°C. Depending on the Si and B content along with the limited solubility in Mo the ratio of Mo to intermetallic phases changes. The alloys being of interest in this study have Mo in solid solution (Mo₃₅) along with the intermetallic compounds Mo₃Si and Mo₅SiB₂ (T2). The T2 phase is rich in B which additionally enhances oxidation resistance. Along with Mo₃Si it forms due to limited B solubility in Mo₃₅. Both intermetallics have a very high melting temperature (>2100°C).

Mo-Si-B alloys suffer from volatilization of Mo oxides. As long as no protective silica scale is formed, this will lead to a continuous mass loss of the substrate. The aim is to decrease the mass loss which causes heavy problems because at temperatures of 600-800°C silica will only grow at a very slow rate and enhances the so-called pesting phenomenon [4]. Efforts in improving the oxidation resistance of three phase Mo-Si-B at elevated temperatures by adding highly reactive elements, e.g. Cr, Al and Ti [5-7], have already been made. In this work the influence of additions in the form of minor additions of oxide dispersions will be investigated.

2. Experimental procedures
The molybdenum silicide alloys were prepared from commercially available powders using a mechanical alloying (MA) route in order to produce a supersaturated Mo₃₅. For a homogeneous distribution of the intermetallic phases within a continuous Mo₃₅ matrix to ensure excellent mechanical properties, after cold-isostatic pressing (CIP) sintering under H₂-atmosphere at 1500°C was applied. The compaction of the sintered material was performed by hot-isostatic pressing (HIP) at 1500°C followed by an annealing step for 10 hours at 1700°C [8,9]. Discontinuous oxidation experi-

Figure 1 Mo-rich corner of the Mo-Si-B phase diagram at 1600°C [3]
ments in laboratory air as well as continuous isothermal thermogravimetric analyses (TGA) using a Sartorius microbalance with a resolution of 1 μg were carried out. The oxide scales were characterized by X-ray diffraction (XRD), surface and cross-sectional SEM in secondary electron (SE) and back-scattered electron (BSE) mode. EDS was used to determine the elements present in the scale qualitatively. Oxidation specimens having the dimensions (10x4x3) mm were machined using wire electro-discharge machining. Prior to oxidation the specimens were ground and polished with SiC paper and ultrasonically cleaned in ethanol. To study the oxidation behaviour, the specimens were placed on alumina boats in such a way that there was only minimal contact with the alumina. For the TGA measurements the specimens were hung on a platinum wire directly connected to the microbalance. The weight and size of each sample were measured carefully before oxidation exposure. The static oxidation consisted of exposing samples for a fixed duration of time in static air in a box furnace, weighing each sample followed by microstructural examination.

For the oxidation tests, four different temperatures were selected. The first temperature was at 750°C, below the sublimation temperature of Mo oxide (>795°C). At 820°C volatilization of Mo oxides easily takes place and at 1100°C up to 1300°C the formation of silica and vaporization of Mo oxide should proceed at a very fast rate. No oxidation testing was carried out in the temperature range 500-700°C and below. It is reported in [10] that only the formation of a Mo oxide layer will occur following a parabolic mass gain. This oxide is going to evaporate immediately when reaching the sublimation temperature.

Table 1 shows the compositions of the alloys of interest in this study. Oxide dispersions of La$_2$O$_3$ and ZrO$_2$ is aimed at an improvement of mechanical properties. La$_2$O$_3$ helps to increase ductility. ZrO$_2$ decreases grain growth (Mo$_{ss} \approx$20%) during sintering in order to obtain higher strength and ductility. In this work implications due to microalloying of La$_2$O$_3$ and ZrO$_2$ on the oxidation behaviour of Mo-9Si-8B were studied.

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<th>Table 1 Compositions of the three alloys (in at.%) investigated in this study</th>
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<td><strong>Mo</strong></td>
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3. Results

3.1 Oxidation behaviour of Mo-9Si-8B

Figure 2 shows the weight change vs. time plot for conventional Mo-9Si-8B at 750°C, 820°C, 1100°C and 1300°C. The time of exposure in a logarithmic scale is shown in minutes. It should be noted that in the weight change axis a scale-break between -125 to -450 mg/cm$^2$ is applied. Figure 3 gives detailed information on the formation of the measured average oxides thickness at 1100°C and 1300°C. Again, the logarithmic timescale has to be noted. The oxidation times and temperatures as well as the scaling of the axis are widely identical to the plots in sections 3.2 and 3.3.
At 750°C, in the initial state of oxidation, single crystallites appear on the specimen surface. XRD analysis identifies them as MoO₃. After 15 minutes the crystallites disappear and a pale yellow-white oxide starts forming on the surface. Mo and Si along with oxygen were detected by EDS analysis in one single layer. The average thickness of this oxide mixture after 15 minutes of oxidation was 18 μm. With increasing exposure time the oxide layer grows to 190 μm after 7 hours having a sponge-like structure (s. Figure 4) covering the whole sample surface and expanding its overall volume. At no time a dense and homogeneous silica layer formed.

Also at 820°C, MoO₃ crystallites initially form on the specimen surface but disappear after 15 minutes. After 7 hours of exposure, areas covered with silica as well as yellow and brown oxide were present on the alloy surface. Two independent oxide layers can be identified (s. Figure 5). The first layer at the substrate/scale interface is MoO₂, SiO₂ forms at the MoO₂/oxygen interface. Single spots of MoO₃ were identified on top of SiO₂. After 7 hours of oxidation the thickness of the MoO₂ scale is measured to be 150-200 μm and 100-600 μm for the silica scale which partially not closes at all. After 72 hours the average thickness of the MoO₂ layer reaches 400-600 μm leading to a valley like silica surface, rich in protrusions.

At 1100°C, initially silica forms (s. Figure 6). Pores and cavities are closed after 5 minutes of oxidation. A second oxide layer being identified in the initial oxidation state at the substrate/scale interface is MoO₂ which disappears after 7 hours of oxidation.
Instead, an area of internal SiO$_2$ is present below the silica scale. The precipitates are embedded in Mo. MoO$_3$ bubbles are present in the silica scale up to 7 hours. At 1300°C in the initial oxidation state the formation of SiO$_2$ with an average scale thickness of 6 µm and a very thin (< 1 µm) MoO$_2$ scale is detected. After 1 hour of exposure time no more MoO$_2$ was found. Similar to the oxidation behaviour at 1100°C, in the initial oxidation state, MoO$_3$ particles can be found within the silica scale but disappear after 7 hours of oxidation. While the formation of silica at 1100°C was almost constant after the initial state, at 1300°C it grows continuous from 4 µm after 5 minutes reaching an average thickness of 25 µm after 72 hours of exposure. Figure 7 shows a homogeneous silica scale along with internal precipitations of SiO$_2$ particles surrounded by Mo without intermetallics phases after 72 hours of oxidation.

3.2 Oxidation behaviour of Mo-9Si-8B-La$_2$O$_3$

Figure 8 shows the weight change vs. time plot for the La$_2$O$_3$-alloyed Mo-9Si-8B. A break in the mass change axis is applied between -150 to -450 mg/cm$^2$. Information about the average oxides thickness of SiO$_2$ and MoO$_2$ at 820°C, 1100°C and 1300°C is given in Figure 9.

Similar to the conventional Mo-9Si-8B, at 750°C, network structures consisting of MoO$_3$ and SiO$_2$ are discovered on the La$_2$O$_3$-alloyed material (s. Figure 10) and the substrate is completely transformed into MoO$_3$ and SiO$_2$ after 72 hours of oxidation.
At 820°C, the sample being oxidized for 5 minutes shows transparent MoO$_3$ crystallites on the surface. After 1 hour, the crystallites have disappeared while silica locally having small cavities has formed over the surface. The cavities vanish after 7 hours of oxidation leaving a homogeneous silica scale with inclusions of MoO$_3$ bubbles. Below the silica, MoO$_2$ of approximately the same scale thickness forms. While the average thickness of the silica scale stays almost unchanged, the MoO$_2$ layer underneath reaches an average value of 52 µm after 72 hours of oxidation. Figure 11 shows an example of the oxide phase arrangement.

At 1100°C, an initial mass loss of 14 mg/cm$^2$ takes place. After 72 hours of oxidation the mass loss is measured to be 15 mg/cm$^2$. An initial thin MoO$_2$ layer with an average thickness of 2 µm has completely disappeared after 1 hour of oxidation. MoO$_3$ in the silica scale was not appreciable after 7 hours of oxidation.

At 1300°C, already after 1 hour, no more MoO$_3$ is present inside the silica scale. After 5 minutes of oxidation, particles of La$_2$O$_3$ can be found on the silica surface which are not discovered at lower testing temperatures. After 72 hours instead of single La$_2$O$_3$ particles, islands have formed out (s. Figure 12). After 7 hours an area of SiO$_2$ precipitations was identified below the MoO$_2$ layer, which is still present after 72 hours, surrounded by Mo (s. Figure 13).
3.3 Oxidation behaviour of Mo-9Si-8B-ZrO₂

Figure 14 shows the mass change behaviour for the ZrO₂-alloyed Mo-9Si-8B with a break in the mass change axis between -350 to -500 mg/cm². Additional average oxides scale thickness information of SiO₂ and MoO₂ at 1100°C is given in Figure 15.

Again at 750°C the mass change behaviour was observed to be almost linear with time. The structure of the oxide layer formed is identical to the conventional as well as the La₂O₃-alloyed material. At 820°C, similar oxidation behaviour as compared to the other alloys was observed – initial formation of MoO₃ crystallites, MoO₂ at the scale/substrate interface, SiO₂ scale on top of MoO₂ and MoO₃ spots imposing SiO₂. At 1100°C just after 5 minutes of oxidation a silica scale covered the alloy, the initial mass loss after 15 minutes (7 mg/cm²) was measured to be half that for the conventional (16 mg/cm²) as well as the La₂O₃-alloyed material (15 mg/cm²). The mass change up to 72 hours of oxidation was almost unaffected (11 mg/cm²). At all times, the silica layer looked very flat and smooth without protrusions or pores. In the initial oxidation state at 1300°C, silica was found all over the substrate surface along with ZrO₂ particles (light spots; s. Figure 16) having an average diameter of 0.5-1 µm. A high content of B appeared to be present on the surface. Just after 5 minutes of exposure the silica covered surface showed pore-like protrusions (white areas; s. Figure 17). These protrusions have an average diameter of 10 µm after 5 minutes, 19 µm after 15 minutes and 65 µm after 1 hour of oxidation.

Figure 14 Weight change vs. time plot for Mo-9Si-8B-ZrO₂

Figure 15 Oxide scale thickness of silica and molybdenum oxide at 1100°C

Figure 16 SE image of Mo-9Si-8B-ZrO₂ surface at 1100°C after 1 hour of oxidation

Figure 17 SE image of Mo-9Si-8B-ZrO₂ surface at 1300°C and 5 minutes of oxidation
Taking a closer look on the protrusions, two different types appear. Figure 18 (a) shows a protrusion found on the surface after 15 minutes of oxidation. Inside the protrusion only SiO₂ exists. In Figure 18 (b) the protrusion is not closed with silica but Mo oxide is present inside. The B concentration is very high on the surface of the oxide layer. Looking at the mass change plot, at all times the mass loss at 1300°C is higher than for the samples being oxidized at 750°C and after 72 hours of oxidation the sample consists only of SiO₂/B₂O₃.

Figure 18 (a) SE image of Mo-9Si-8B-ZrO₂ surface at 1300°C and 15 minutes of oxidation

Figure 18 (b) SE image of Mo-9Si-8B-ZrO₂ surface at 1300°C and 15 minutes of oxidation

4. Discussion
For all alloy compositions examined in this study in the initial oxidation state (<15 minutes), a strong mass loss occurs. This is because the volatilization of MoO₃ takes place until the dense formation of silica which protects the alloy from further evaporation. Minimizing the initial mass loss is crucial for the designing of the alloys. At 750°C all three alloy compositions experienced almost linear mass loss with increasing exposure time leaving only MoO₃ and SiO₂. The evaporation of MoO₃ is rate determining since at no time of the oxidation process the formation of a protective silica layer was found, even though from the thermodynamic point of view the formation of boria-silica-glass is preferred (s. Figure 19).

Figure 19 Oxygen activity vs. temperature phase diagram for Mo-9Si-8B
4.1 Oxidation behaviour of Mo-9Si-8B
The basic mechanisms behind the oxidation of conventional Mo-Si-B alloys are well understood. Up to 450°C MoO\textsubscript{3}, B\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} are in solid state. MoO\textsubscript{2}, the low oxygen activity form of MoO\textsubscript{3}, only grows underneath the silica layer. At temperatures beyond 450°C, B\textsubscript{2}O\textsubscript{3} turns into liquid state. MoO\textsubscript{3} will turn into liquid state at temperatures beyond 795°C.

At 750°C XRD analysis showed the presence of MoO\textsubscript{3} at all oxidation times while no MoO\textsubscript{2} is present. This indicates that the mixed oxide layer consisting of MoO\textsubscript{3} and SiO\textsubscript{2} is offering enough fast pathways and porosity for oxygen so the low oxygen partial pressure phase MoO\textsubscript{2} will not occur. The formation of silica is not sufficient to protect the alloy. Parthasarathy et al. [10] believe that the B-content in the scale is responsible for the poor oxidation resistance at 750°C.

At 820°C the evaporation of MoO\textsubscript{3} is accelerated allowing the SiO\textsubscript{2} to form a dense layer at the scale/oxygen interface. With the help of B, a B\textsubscript{2}O\textsubscript{3}-containing silica forms slowing down oxidation kinetics. Yet, no parabolic rate law is discovered, since the oxidation kinetics is not just oxygen diffusion controlled throughout the whole sample. MoO\textsubscript{3} crystallites randomly distributed over the SiO\textsubscript{2} layer are a sign of leakage in the silica scale. The reason is seen in the fluidity of the B-rich silica layer which changes drastically with only small additions in B\textsubscript{2}O\textsubscript{3} [11]. Still oxygen can penetrate through the layer easily allowing the development of MoO\textsubscript{2} which forms faster than it permeates through the silica evaporating as MoO\textsubscript{3}. As a consequence, the thickness of the MoO\textsubscript{2} layer at the scale/substrate interface increases, eventually leading to local but strong expansion, breaking and spalling the silica scale. This opens new fast pathways, first to the MoO\textsubscript{2} layer below the silica. MoO\textsubscript{2} transforms into MoO\textsubscript{3} and evaporates. Eventually, spalling might allow oxygen to react with the Mo\textsubscript{ss} to form new MoO\textsubscript{3} from the substrate itself.

At 1100°C the volatilization rate of B\textsubscript{2}O\textsubscript{3} is 1 mg/cm\textsuperscript{2}/h. The scale is expected to be very low in B\textsubscript{2}O\textsubscript{3} content. The fluidity of the silica scale is strongly decreased and kinetics mainly controlled by oxygen diffusion through the silica scale. At 1300°C full coverage of the surface by fluxing silica is obtained with the help of B\textsubscript{2}O\textsubscript{3}. It begins to evaporate as soon as it forms due to a high volatilization rate of \approx 5 mg/cm\textsuperscript{2}/h at 1300°C. Respective values are 0.05 and 0.5 mg/cm\textsuperscript{2}/h at 800 and 1000°C [10]. B\textsubscript{2}O\textsubscript{3} evaporation leads to a silica layer with a highly decreased oxygen diffusivity and slow scale growth kinetics, as compared to the scale growth at 820°C. As the cross section in Figure 7 shows after 72 hours, no MoO\textsubscript{3} bubbles are present inside the silica, the permeation of MoO\textsubscript{3} through the silica has stopped and only oxygen diffusion is rate-determining.

4.2 Oxidation behaviour of Mo-9Si-8B-La\textsubscript{2}O\textsubscript{3}
Looking at the mass change curve in Figure 8 and comparing it to the conventional Mo-9Si-8B alloy it becomes obvious that two impressive improvements in the oxidation behaviour of La\textsubscript{2}O\textsubscript{3}-containing Mo-9Si-8B can be stated. The first is at temperatures around 820°C, the second improvement happens at very high temperatures. While adding oxide dispersions in the form of La\textsubscript{2}O\textsubscript{3}, two possible effects need to be considered: (1) active element effects, (2) formation of a La-rich boria-silica scale.

4.2.1 Active element effects
Active element effects occur through the improvement in oxidation resistance of high temperature alloys as a result of addition of dispersions of stable oxides. Two effects have been identified to be important. Firstly, scale adhesion increases which is
especially helpful for cyclic oxidation, secondly the growth rate of the oxide can be reduced. The essential mechanisms for the improvement of the oxidation through oxide dispersions can be doping effects, formation of a blocking layer in the scale or short-circuit diffusion [12]. Alloys containing a dispersoid reach steady state oxidation much earlier than the dispersion-free alloys. This was observed in this study for the La$_2$O$_3$-containing alloy. Figure 19 shows one example for a TGA experiment being carried out at 1000°C. After long term oxidation the overall mass loss for the La$_2$O$_3$-containing alloy is about 4 mg/cm$^2$ higher than for the conventional alloy. However, it approaches steady state oxidation after 60 hours while the conventional alloy keeps losing mass. This effect is even more drastic at 820°C. Already after 6 hours steady state oxidation was approached.

![Figure 19 TGA measurement for Mo-9Si-8B(-La$_2$O$_3$) at 820°C and 1100°C](image)

After the initial mass loss, the grain boundaries seem to act as a natural barrier for the outward diffusion of silicon through the phase boundaries. After 72 hours of oxidation at 1300°C, the depth of internal SiO$_2$ precipitations is 3.5 times higher (89 µm) than for the conventional alloy using the same testing parameters (26 µm).

4.2.2 Lanthanum rich boria-silica scale formation

Another reason for the improvement in the oxidation resistance, especially at 820°C, is seen in the formation of a La-containing boria-silica glass with an extremely small thermal expansion coefficient. The high values of the glass transformation temperature and viscosity at ambient conditions suggest that these glasses have a very coherent network with few, if any, nonbridging oxygen or other interruptions. The networks must be very dense so the glass has little free volume compared to vitreous boric oxide [13]. For glasses containing more than 22 at. % La$_2$O$_3$ the formation of the crystalline phase LaB$_3$O$_6$ is suggested [14]. In general La helps to decrease the fluidity of the boria containing silica. Still it will be more fluid than pure SiO$_2$. This explains the growth of MoO$_2$ below the silica scale which can not be stopped at 820°C. The high amounts of La$_2$O$_3$ in the form of islands which were discovered on the sample surface at 1300°C are thought to occur because of a phase separation upon cooling. The formation of a hydroxide along with water at room temperature is also possible, but the experiment took place at normal atmospheric conditions. The influence of La$_2$O$_3$ dispersions is the most effective at 820°C. While linear mass loss was discovered for the conventional as well as the ZrO$_2$-containing alloys, mass
change follows at a parabolic rate law in the La₂O₃-alloyed material. Obviously with the third-element addition, oxygen diffusion through the silica scale can be drastically reduced as seen from the average thickness of the MoO₂ layer after 72 hours of oxidation (50 µm). At that time, the conventional alloy already showed an average MoO₂ layer thickness of 400-600 µm. With the slower growth rate of MoO₂ the heavy deformations of the SiO₂ layer is suppressed. At 1300°C, while comparing with the conventional alloy, the evaporation of MoO₃ in the initial oxidation state was less pronounced. It is thought that La₂O₃ particles segregating to the grain boundaries lead to reduced grain boundary transport rates, resulting in decreased mass loss rates. At 1300°C this is indeed happening. A comparison with the mass loss behaviour for the La₂O₃-alloyed material shows that the rate is always slower than that of the conventional alloy.

4.3 Oxidation behaviour of Mo-9Si-8B-ZrO₂

From the thermodynamic point of view ZrO₂ is extremely stable. The formation of zirconium molybdates, borides or silicides is not expected as well as the dissociation of ZrO₂ or dissolution in the matrix. This assumption can be directly supported by thermodynamic equilibrium calculations. The reaction between SiO₂ and ZrO₂ forming ZrSiO₄ which is reported in [15] is also not expected, since it will only occur at temperatures beyond 1500°C. This leads to the assumption that ZrO₂ itself has no direct effect on the oxidation behaviour. The only difference to the conventional alloy is seen in the finer distribution of the phases. At 750°C and 820°C there is no significant difference in the oxidation behaviour of Mo-9Si-8B containing ZrO₂ and without ZrO₂. At 1100°C, with the help of B, along with the fine microstructure, the silica scale forms having less mass loss than the conventional alloy. Because of the finer distribution of the phases Mo₃s is surrounded by more intermetallic phases which develop a silica scale very fast at this temperature. The alloy surface can be closed faster than for the conventional alloy, after 5 minutes of oxidation the silica scale thickness will almost stay unaffected. This explains why the surface looks very smooth without having any protrusions or pores. Oxygen diffusion proceeds at a very slow rate, after 72 hours no more MoO₂ is present. The fluxing of the silica is faster than the formation of cavities due to evaporation of MoO₃. Comparing the mass loss data, the alloy containing ZrO₂ should oxidize at a lower rate, which is in fact true. At all states of oxidation the mass loss showed the lowest rate. The same effect but at 1300°C leads to the complete desintegration of the sample. Since the phases are distributed much finer than for the conventional alloy, the evaporation of MoO₃ will take place not only from the surface but through the phase boundaries. B₂O₃ at 1300°C is evaporating at a very fast rate. It takes longer to close open pores. This is also one reason why in the initial oxidation state a higher mass loss compared to the mass loss at 1100°C is present. While pores are closing, evaporation takes place simultaneously through the phase boundaries. The finer microstructure has more phase boundaries, the probability for the formation of pores which are not closing is higher for the conventional material. Some pores will of course close, others might close only at the walls still providing oxygen access to the bulk material. Once the access into the bulk is provided, volatilization of MoO₃ will work its way down into the substrate. Looking into these pores, Mo is seen present, revealing a direct pathway to the substrate without protection by SiO₂ in this area. The key appears to be the initial formation of the pores. With increasing exposure time the diameter of the pores increases. The more grains/phase boundaries, the higher the probability of the formation of open pores, once the oxidation has an open path into the substrate. Of course B helps to close
pores in the initial state but the distribution of the phases is too small. The effect of a smaller microstructure is also noticeable at 750°C. At all times of oxidation mass loss rate was 2-5 times faster than for the conventional alloy as a consequence of enhanced evaporation through the phase boundaries.

5. Conclusions
In this study two important factors for a further improvement of the oxidation behaviour of Mo-Si-B alloys were studied. The first aspect dealt with is the oxidation resistance of Mo-Si-B alloys at moderate temperatures. In the temperature range of 750-820°C, the formation of two competing oxides (SiO₂, MoO₃) excludes the formation of a homogeneous silica scale. The formation of MoO₂ and the damage of the silica scale is drastically reduced by lowering the oxygen diffusity through the silica scale at 820°C and above as a consequence of adding La₂O₃. All Mo-9Si-8B alloys show excellent oxidation resistance in the temperature regime around 1100°C except of an initial mass loss, which is the second important factor. It has to be said the initial mass loss will occur at any oxidation temperature. ZrO₂ addition to Mo-Si-B seems to have no direct effect on the oxidation behaviour but due to the finer microstructure formed, different oxidation behaviour as compared to the conventional alloy was identified which is especially helpful at temperatures around 1100°C, but detrimental at temperatures around 1300°C. Already at 1300°C for the conventional Mo-Si-B, B was found to evaporate very fast in the initial state of oxidation leading to heavy weight loss. The process stops if the oxide layer is sealed after initial heavy evaporation. The important regime for the further development of Mo-Si-B alloys is the temperature range of applications between 650 and 900°C. By means of La₂O₃ microalloying, improvements in the temperature range from 800 to 900°C were found to be possible. At 1100°C with the help of ZrO₂ and a finer microstructure the initial mass loss could drastically be reduced, this effect will be gone at 1300°C because of microstructure effects and high evaporation rates of B.

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References