

**Author's Version**

**Magnetron sputtered silicon coatings as oxidation protection for Mo-based alloys**

by

**Ronja Anton<sup>1,\*</sup>, Nadine Laska<sup>1</sup>, Uwe Schulz<sup>1</sup>, Susanne Obert<sup>2</sup>, Martin Heilmaier<sup>2</sup>**

<sup>1,\*</sup> German Aerospace Center (DLR), Institute of Materials Research, Linder Hoehe, 51147 Cologne, Germany

E-mail: ronja.anton@dlr.de

<sup>2</sup> Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Engelbert-Arnold-Straße 4, 76131 Karlsruhe, Germany

Advanced Engineering Materials (2020)  
<https://doi.org/10.1002/adem.202000218>

**Magnetron sputtered silicon coatings as oxidation protection for Mo-based alloys**

*Ronja Anton<sup>1,\*</sup>, Nadine Laska<sup>1</sup>, Uwe Schulz<sup>1</sup>, Susanne Obert<sup>2</sup>, Martin Heilmaier<sup>2</sup>*

<sup>1,\*</sup> German Aerospace Center (DLR), Institute of Materials Research, Linder Hoehe, 51147 Cologne, Germany

E-mail: ronja.anton@dlr.de

<sup>2</sup> Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WK), Engelbert-Arnold-Straße 4, 76131 Karlsruhe, Germany

**Keywords:** Magnetron sputtering, Si based coatings, thermally grown silica, oxidation behavior, interdiffusion processes

Mo-based alloys with solidus temperatures around and above 2000 °C are attractive high temperature structural materials for future applications in the hot section of gas turbines. However, their oxidation behavior is poor due to pesting starting at 600 °C and non-protective oxide growth at temperatures above 1000 °C. To ensure a sufficient oxidation resistance over a wide temperature range, protective coatings become inevitable. In the present work, silicon coatings have been applied by magnetron sputtering on Mo-9Si-8B and on TZM. The coating architecture was designed to minimize the inter-columnar gaps and porosity, thereby increasing the density. Specimens were tested at 800 °C and 1200 °C in air isothermally for up to 300 hrs. The focus was put on the chemical reactions at the coating-substrate interface, the phase formation and on the evolution of the thermally grown oxide. An initially globular SiO<sub>2</sub> evolves into a uniform SiO<sub>2</sub> layer providing excellent oxidation protection. The investigations revealed a rather slow interdiffusion between the coating and the alloys when tested in air. At the coating-substrate interface exclusively the Mo<sub>3</sub>Si phase develops. Finally,

the phase formation at the coating-substrate interface was studied in detail for various heat treatments in air and in vacuum.

## 1. Introduction

The efficiency of a gas turbine can be improved by increasing the gas inlet temperature <sup>[1-3]</sup>. Nowadays, aero-engines are limited by the temperature capability of the materials used in the first stages of the high-pressure turbine. Ni-based superalloy blades are provided with internal cooling and coatings consisting of an outer thermal barrier layer and a bond coat to connect it to the respective substrate. Although they show excellent performance, a further increase in operating temperature with this material is unlikely due to the limit given by the solidus temperature of Ni-base superalloys <sup>[2, 3]</sup>. Mo-based alloys with solidus temperatures around and above 2000 °C are attractive high temperature structural materials to overcome those limits. Therefore, these alloys are potential candidates for future applications in the hot section of gas turbines. Alloys with a composition in the three phase field Mo<sub>ss</sub>, Mo<sub>3</sub>Si and Mo<sub>5</sub>SiB<sub>2</sub> show favorable mechanical properties <sup>[2-4]</sup>. Mo<sub>ss</sub> forms a continuous matrix that provides sufficient fracture toughness while the intermetallic phases Mo<sub>3</sub>Si and Mo<sub>5</sub>SiB<sub>2</sub> ensures promising creep resistance. Their low tensile ductility at room temperature and oxidation behavior are still challenging. The oxidation as well as the creep behavior of these alloys can be somewhat improved by alloying with titanium <sup>[5-8]</sup> which is also the topic of a companion paper in the same issue (see Matthias Weber et al., Effect of Water Vapor on the Oxidation Behavior of the Eutectic High-Temperature Alloy Mo-20Si-52.8Ti, this issue). However, the general oxidation behavior of Mo-based alloys is poor due to evaporation of MoO<sub>3</sub> at temperatures below 1000 °C, well known as the pesting regime <sup>[9]</sup>, and rapid oxide growth at temperatures above 1000 °C. To ensure a sufficient oxidation resistance over a wide temperature range, protective coatings become inevitable. A thermochemical compatible

interface between coating and alloy as well as a coefficient of thermal expansion which is close to that of the Mo-alloys are prerequisites for a good coating performance. Substantial improvements could be demonstrated by Mo, Si and B containing coatings applied by chemical (CVD) or physical vapor deposition (PVD) techniques. The CVD coatings were produced by co-pack cementation of Si, Si and B, or Si and Al. After heat treatments and testing the coatings mostly show either an oxidation protection based on silicon dioxide, on borosilicate or on  $\text{Al}_2\text{O}_3$  [10-13]. The magnetron sputtered PVD coatings with a thickness of around 5 to 10  $\mu\text{m}$  developed in our previous work showed promising oxidation behavior. Three-phase coatings consisting of  $\text{Mo}_5\text{Si}_3$ ,  $\text{MoSi}_2$  and  $\text{MoB}$  as well as single-phase  $\text{MoSi}_2$  and  $\text{MoB}$  coatings have been investigated.  $\text{Mo}_5\text{SiB}_2$  (T2) was introduced as diffusion barrier due to its high atomic packing density and to avoid early coating degradation by inter-diffusion with the alloy [2, 14]. In addition, aluminum containing coatings based on Mo-70Al and Mo-47Si-24Al have been investigated as well including the application of thermal barrier coatings on top [15].

In this research, a different approach has been chosen. In order to establish a larger coating thickness by magnetron sputtering, boron was avoided in the procedure since it possesses a poor sputter rate. Furthermore, a one layer concept was pursued for simplification. Silicon is widely accepted as oxidation protection layer and used by various researchers for SiC/SiC CMCs as a bond coat in environmental barrier coating systems [16, 17]. Therefore, Si has been used as a PVD coating to protect Mo-based alloys. Its oxide  $\text{SiO}_2$  can emerge in various polymorphs - in most studies cristobalite is found. This so-called thermally grown oxide (TGO) is one of the slowest forming oxides known to date being able to withstand several thousand hours of oxidation at temperatures above 1100 °C. Moreover, silicon shows favorable mechanical properties since it becomes ductile at temperatures above 600 °C [18, 19]. The main emphasis of this study is to develop and characterize a single layer coating based on silicon for the Mo-9Si-8B alloy in order to ensure oxidation protection up to 1200 °C.

## 2. Experimental

The Mo-based alloy (Mo-9Si-8B in at%) was fabricated at Karlsruhe Institute of Technology (KIT) by arc melting the high-purity elements Mo, Si and B with respective purities of 99.99, 99.8 and 99 %. An arc-melter of type AM/0,5 by Edmund Buehler GmbH was used and the arc-melting procedure was performed in a water-cooled copper crucible under Ar atmosphere as described in detail by Obert et al. in Ref. <sup>[20]</sup>. During arc melting of various Mo-Si-X alloys the contamination by oxygen was routinely measured by hot gas carrier extraction. Typically, between 150 and 350 wt. ppm were detected which is substantially lower as the values observed in PM processed material being above 2000 wt. ppm <sup>[21]</sup>. A homogenous elemental distribution was ensured by repeating the melting procedure multiple times and the final chemical composition was confirmed to vary less than 0.5 wt% from the weighed in target chemical composition. As expected from the phase diagram, the produced Mo-9Si-8B alloy consists of the phases Mo<sub>ss</sub> (bcc), Mo<sub>3</sub>Si (A15) and Mo<sub>5</sub>SiB<sub>2</sub> (T2) <sup>[22]</sup>. For the coating trials the alloy was used in the as-cast state with substrate dimensions of 10 x 15 x 2 mm. For comparison, a commercial Titan-Zirconium-Molybdenum alloy (TZM) with the nominal composition of Mo-0.5 Ti-0.08 Zr-0.01–0.04 C (in at%) provided by Plansee AG, Reutte, Austria has been used as well.

The Si-coating was applied using a batch-type magnetron sputtering facility (Z400, Systec SVS vacuum coatings, Karlstadt, Germany). Before coating deposition, specimens were cleaned by Ar<sup>+</sup>-ion etching to activate the specimen surface. Two dense polycrystalline disks of Si with a diameter of 100 mm were utilized as targets that were placed in a face-to-face arrangement. DC sputtering was performed at 1 kW target power to achieve a total thickness of the coating between 25 μm and 50 μm. After first successful tests with a 50 μm thick Si-coating, the thickness has been halved since the interdiffusion between coating and Mo-Si

substrates was slower than expected. The majority of the experiments have been carried out on the thinner coatings. The total pressure during deposition was 0.45 Pa in Ar atmosphere (flow rate at 25 sccm). During the deposition process the substrate temperature reached about 100 °C without additional heating. The deposition rate was around 6 µm/hrs. Samples were constantly rotated during the application of the coating ensuring a full coverage of the samples by the coating and a nearly all-around constant thickness. Due to variation in sample position with respect to the sputtering source a slight variation in coating thickness was noticeable.

As the Si-coating was X-ray amorphous after the deposition process, a crystallization treatment was applied for 1 hr at 900 °C in air. In order to achieve a nearly dense coating and to rapidly close the inter-columnar gaps, the specimen underwent a rapid heating up during crystallization as well as during the initial oxidation. This temperature was chosen to guarantee the crystallization of Si which was confirmed by high temperature XRD investigations, and to compare the present results to previous data obtained on similar coatings applied on SiC substrates. Afterwards, the coated specimens underwent isothermal oxidation testing up to 300 hrs in lab air in a box furnace. Two temperatures have been used for testing, 800 and 1200 °C, to investigate both, pesting and high temperature oxidation behavior. The crystallization treatment and isothermal oxidation have been performed without a cooling period in between. In order to compare the phase formation at the interface between coating and alloy in vacuum ( $10^{-5}$  mbar) and in lab air, a comparison study has been done with silicon coated TZM.

For all coatings phase analyses were performed using X-ray diffraction (XRD) (Bruker D8 Advance, Cu-K $\alpha$  radiation, EVA/Topas 4.2 software package, Bruker AXS, Karlsruhe, Germany). Microstructural analyses were carried out by scanning electron microscopy (SEM) (DSM Ultra 55, Carl Zeiss NTS, Wetzlar, Germany) equipped with an energy dispersive X-ray spectroscopy (EDS) system (Aztec, Oxford Instruments, Abingdon, UK). EDS analyses

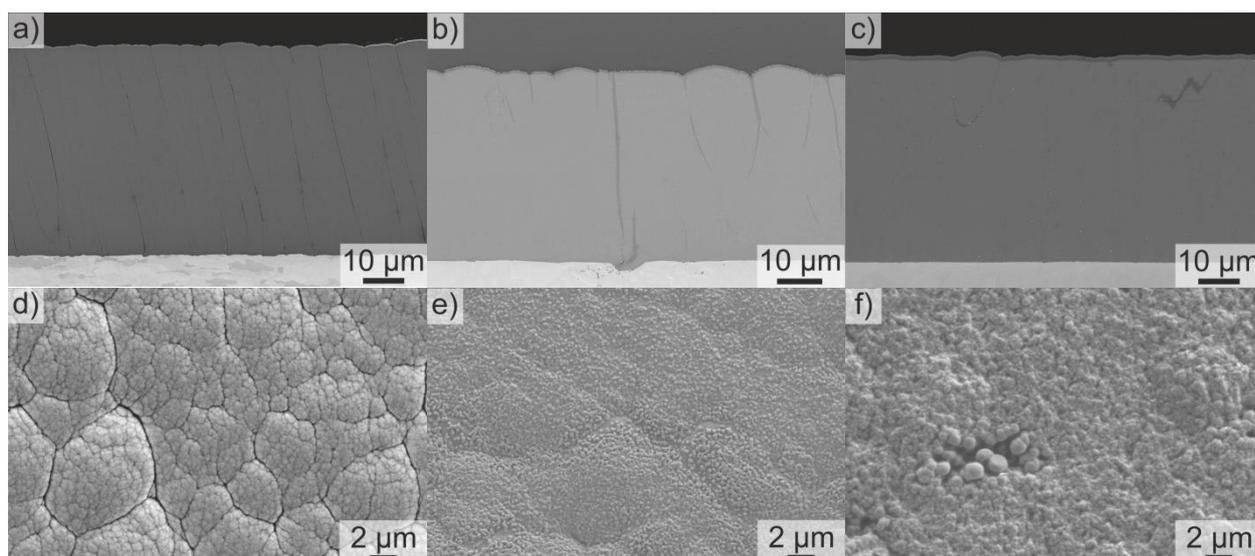
have been performed at 15 kV. For further analysis, two lamellae were produced by a focused ion beam (FIB) (Dual Beam FEI Helios, FEI Philips, Netherlands). In order to analyze the interdiffusion zone (IDZ), transmission electron microscopy (TEM) has been carried out using imaging, EDS analyses, and electron diffraction measurements applying selected area diffraction (SAD) (Tecnai F30 TEM/STEM FEI Philips, Netherlands).

### 3. Results

#### 3.1. Isothermal oxidation behavior of the Si-coated Mo-based alloys

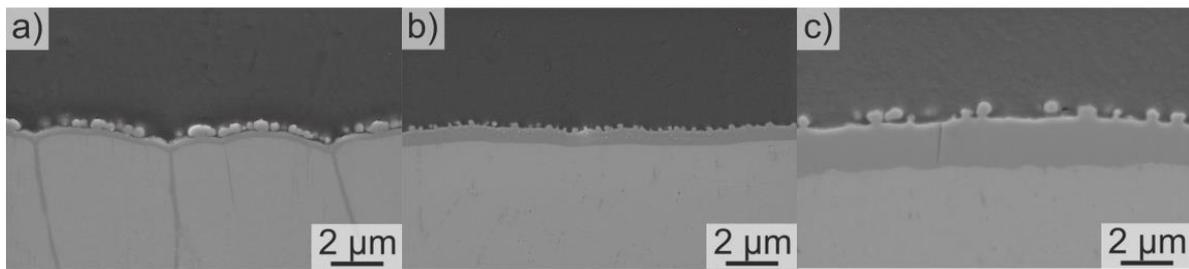
The as-coated silicon coating possesses excellent adhesion on both substrate alloys. It has a columnar structure evident in cross section and a cauliflower pattern in top view, see **Figure 1 a)** and **Figure 1 d)** for the TZM alloy substrate. This specimen serves as a reference micrograph in order to compare the tested coating to the initial as-coated state after the deposition. X-ray diffraction, not shown here, proofed that the coatings were amorphous in this state. After the initial heat treatment for one hour at 900 °C in lab air the Si-coatings crystallized.

In **Figure 1 b)**, the coating is shown after 1 hr of crystallization annealing at 900 °C and 10 hrs of isothermal testing at 1200 °C in air. The SEM cross section in **Figure 1 b)** reveals that inter-columnar gaps get closed already after 10 hrs of exposure due to the oxidation of silicon. A dense SiO<sub>2</sub> TGO is visible on top of the surface of the coating which shows also a bubbly structure, see **Figure 1 e)**. After 100 h heat treatment the only change in the coating system is the obvious growth of the SiO<sub>2</sub> TGO that increased in thickness up to 1.1 μm (**Figure 1 c)**). The top view shows smaller bubbles of SiO<sub>2</sub> that appear now fully dense, see **Figure 1 f)**.

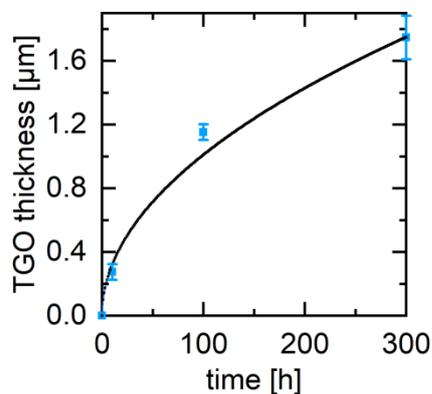


**Figure 1** Silicon coating on Mo-based alloys; a) to c) cross sections and d) to f) top views. a) and d) TZM substrate in the as-coated state; b) and e) Mo-9Si-8B substrate isothermally tested for 10 hrs at 1200 °C; c) and f) Mo-9Si-8B substrate isothermally tested for 100 hrs at 1200 °C.

In Figure 1 b) and c) the formation and growth of a thermally grown oxide is evident after 10 hrs and 100 hrs testing at 1200 °C on Mo-9Si-8B. By analyzing the thicknesses of the TGO with increasing time which is exemplified in **Figure 2 a)** until 10 hrs, **b)** until 100 hrs and **c)** until 300 hrs, a parabolic growth rate of the thermally grown SiO<sub>2</sub> can be confirmed (see **Figure 3**). The SiO<sub>2</sub> consists of the cristobalite phase which has been proven by XRD. The TGO was dense and the initially formed bubbles appeared to be connected to the dense layer forming afterwards. The bubbles were not included in the determination of the TGO thickness.

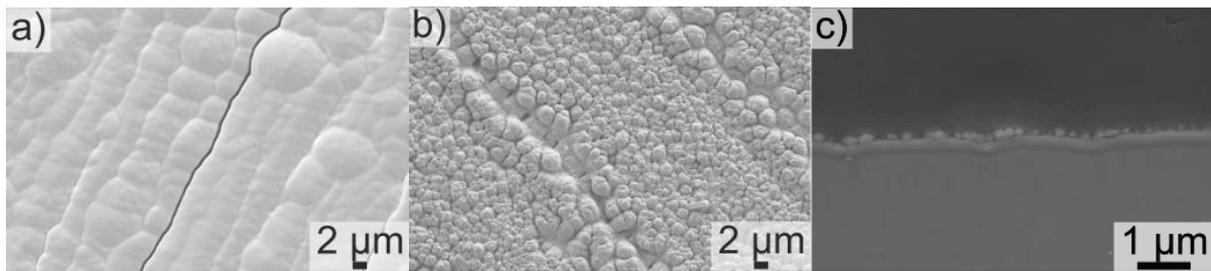


**Figure 2** Formation of the thermally grown oxide consisting of SiO<sub>2</sub> with SiO<sub>2</sub> bubbles on a Si-coating on a Mo-9Si-8B substrate during isothermal testing for; a) 10 hrs; b) 100 hrs; c) 300 hrs at 1200 °C in lab air.



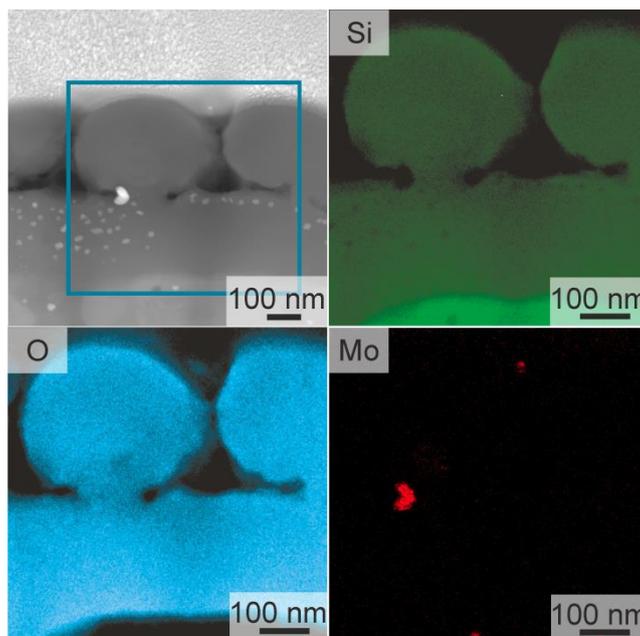
**Figure 3** Growth rate of the thermally grown SiO<sub>2</sub> layer versus exposure time at 1200 °C in lab air.

In order to investigate the potential influence of boron on the formation of the SiO<sub>2</sub> bubbles, oxidation of the silicon coating has been also investigated using a TZM substrate which contains no boron. **Figure 4 a)** shows that after a crystallization treatment at 900 °C for 1 hour and 30 minutes at 1200 °C, both done in air, no bubble shaped structures were visible on the surface. After a total oxidation time of 2 hrs at 1200 °C the surface is covered by bubbles that appear similar to the morphology formed on Mo-9Si-8B, seen in **Figure 4 b)**. Again, the bubbles are well connected to the dense silica layer that forms underneath during prolonged oxidation of 5 hrs (see **Figure 4 c)**).



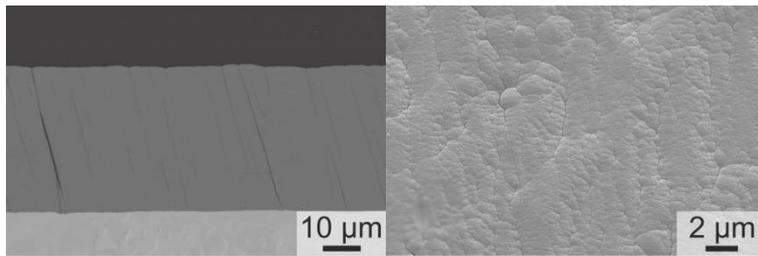
**Figure 4** SEM pictures of the silicon coating surface on TZM substrates tested for; a) 1 hr at 900 °C and 30 min at 1200 °C in air; b) 2 hrs at 1200 °C in air showing a bubbly SiO<sub>2</sub> structure; c) 1 hr 900 °C and 5 hrs at 1200 °C in air showing the bubbly structure in the cross section.

The TEM-EDS mapping in **Figure 5** shows a FIB lamella of the 10 hrs tested silicon coating on a Mo-9Si-8B substrate. The silicon coating is clearly visible as well as the SiO<sub>2</sub> TGO. A weak molybdenum signal is detectable in some isolated areas. There is no clear accumulation of Mo within the bubbles, although some Mo signals appear locally in the gaps between the silica bubbles.



**Figure 5** TEM-EDS mapping of the TGO done on a FIB lamella of the 10 hrs isothermal tested silicon coating on a Mo-9Si-8B substrate at 1200 °C.

To additionally investigate the potential impact of MoO<sub>3</sub> sublimation that starts at about 700 °C on the coating behavior, an isothermal heat treatment has been applied at 800 °C for 100 hrs after the crystallization treatment for 1 hr at 900 °C. The result shown in **Figure 6** reveals a relatively dense coating on a Mo-9Si-8B substrate without a visible TGO. A few columns do not seem to be sealed by SiO<sub>2</sub> but do not lead to oxidation of the substrate. The top view shows a quite dense coating replicating the substrate roughness and showing remaining signs of the typical PVD columnar structure, but to a much lower degree compared to the as-coated condition shown in Figure 1 a) and d). SEM-EDS (not shown here) proofed that no Mo is detected in the coating.

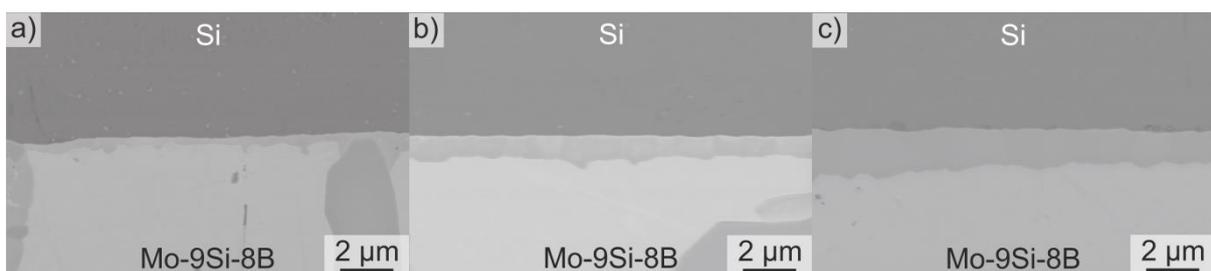


**Figure 6** Silicon coated Mo-9Si-8B substrate isothermally tested for 100 hrs at 800 °C (cross section left and top view right).

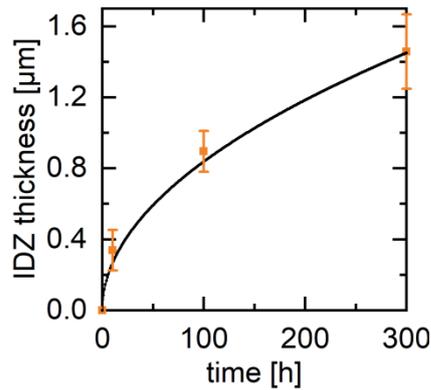
### 3.2. Reaction between coating and substrate during isothermal oxidation

During oxidation an interdiffusion zone (IDZ) can be observed that slowly grows with time.

**Figure 7** shows the increase in thickness of this zone after 10 hrs (**a**), 100 hrs (**b**) and 300 hrs (**c**) at 1200 °C testing temperature. The growth rate of the IDZ versus the exposure time is presented in **Figure 8** where it follows a parabolic growth rate. Although some pores appear at the interface between substrate and coating after 300 hrs, mainly located within the silicon in contact to the IDZ, the adhesion of the coating is still strong which assures the oxidation protective potential of the Si-coating for the Mo-9Si-8B alloy.

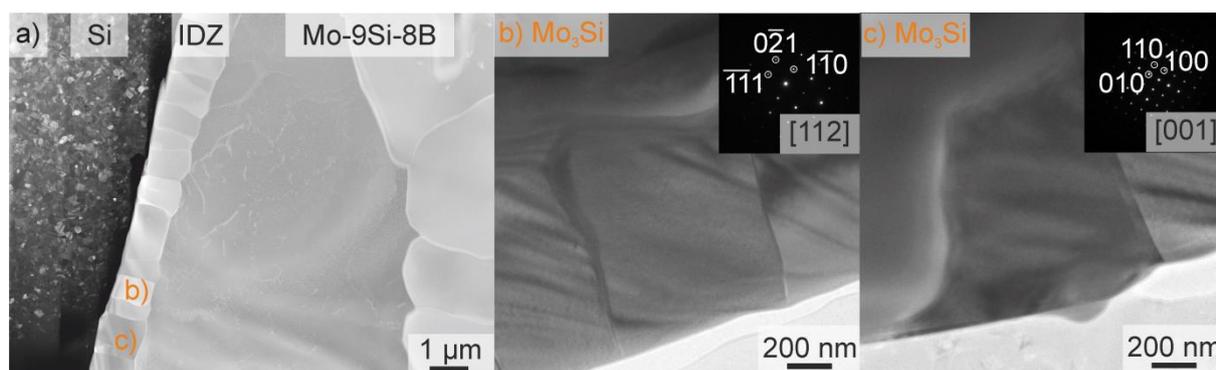


**Figure 7** Interdiffusion zone of a silicon coating on a Mo-9Si-8B substrate isothermally tested for; a) 10 hrs; b) 100 hrs; c) 300 hrs at 1200 °C.



**Figure 8** Growth rate of the interdiffusion zone between silicon coating and Mo-9Si-8B substrate versus the exposure time to 1200 °C in lab air.

In order to clarify which phases have formed at the interface and in the IDZ, a sample tested for 300 hrs was analyzed in the TEM in different locations, see **Figure 9**. **Figure 9 a)** shows a high-angle annular dark-field image (HAADF) of the FIB lamella with the region of interest. The analysis clearly proves that the interdiffusion zone consists exclusively of the  $\text{Mo}_3\text{Si}$  phase. Therefore, two grains have been analyzed in **Figure 9 b)** and **Figure 9 c)**. Comparing two different lamellae yielded that the IDZ is rather inhomogeneous in thickness. In Figure 9 the IDZ thickness is characterized directly by the  $\text{Mo}_3\text{Si}$  grain size since it consists only of one grain in thickness while in other parts several  $\text{Mo}_3\text{Si}$  grains are forming above each other further into the substrate, thereby resulting in a thicker IDZ.



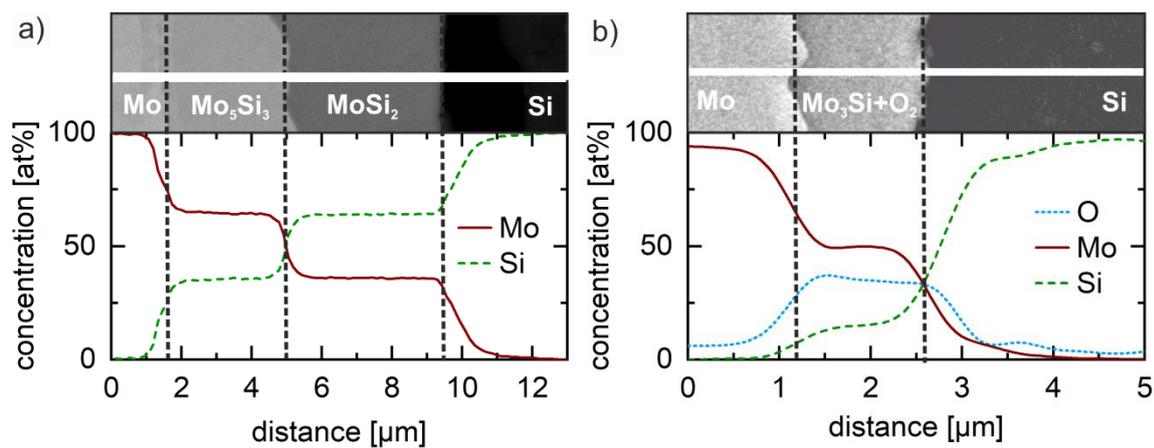
**Figure 9** TEM picture of the silicon coated Mo-9Si-8B lamella isothermally tested for 300 hrs at 1200 °C; a) HAADF overview of lamella with interdiffusion zone; b) grain b within interdiffusion zone and diffraction pattern; c) grain c within interdiffusion zone and diffraction pattern with viewing directions.

Most of the investigations in literature about the interdiffusion of silicon and molybdenum are done with the pure elements under vacuum [23]. In order to separate the phases within the IDZ clearly from the phases in the substrate and for a better comparison with the literature, further investigations have been done on TZM coated with silicon. To study the influence of the annealing atmosphere on the interdiffusion behavior, a vacuum heat treatment was compared to a lab air heat treatment, applying the same time and temperature.

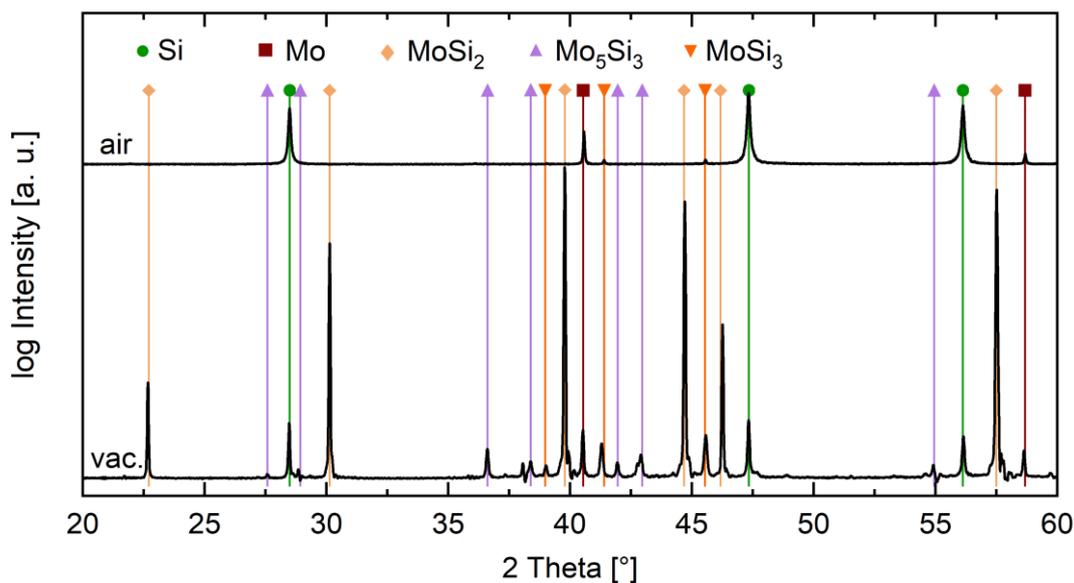
After vacuum annealing for 1 hr at 900 °C and 5 hrs at 1200 °C, the phases  $\text{Mo}_5\text{Si}_3$  and  $\text{MoSi}_2$  evolved to form the IDZ, see **Figure 10 a**). Furthermore, most of the original Si-coating spalled off this IDZ leaving it exposed to the atmosphere. In the EDS line scans using SEM, **Figure 10**, substrate, IDZ and coating were analyzed. The sample annealed in air shows the same IDZ already found in Figure 7. There, the line scan (**Figure 10 b**) illustrates the formation of  $\text{Mo}_3\text{Si}$  in the IDZ. Furthermore, it reveals an oxygen content of about 38 at% (measured by EDS) in the IDZ of the specimen tested in air while there was no oxygen found in the IDZ of the vacuum annealed sample (Figure 10 a)). **Figure 11** provides results of the XRD investigation. Since the Si-coatings used for this investigation were intentionally only

25  $\mu\text{m}$  thick, the XRD information extracted from those samples also provide results on the phases within the IDZ located underneath the Si. Thus, diffraction peaks of the  $\text{Mo}_3\text{Si}$  phase are also present for the air tested sample while the  $\text{Mo}_5\text{Si}_3$  phase is detectable for the vacuum tested sample. Due to the small peak heights of those phases Figure 11 is represented with a logarithmic scale.

Obviously, different phases developed within the IDZ after the vacuum ( $\text{MoSi}_2$ ,  $\text{Mo}_5\text{Si}_3$ ) and the lab air ( $\text{MoSi}_3$ ) treatment as confirmed by EDS and XRD. The development of  $\text{Mo}_5\text{Si}_3$  and  $\text{MoSi}_2$  in the IDZ is conclusive for the vacuum annealed specimen. For the lab air treated specimen the interdiffusion phase shows exclusively the composition of  $\text{Mo}_3\text{Si}$  and some excess oxygen.



**Figure 10** SEM-EDS line scans of the silicon coated TZM substrate tested for 1 hr at 900 °C and 5 hrs at 1200 °C; a) in vacuum; b) in air.



**Figure 11** XRD scan of the silicon coated TZM substrate tested for 1 hr at 900 °C and 5 hrs at 1200 °C in air and vacuum.

## 4. Discussion

### 4.1. Oxidation of silicon on molybdenum based-alloys

The applicability of silicon as an oxidation protective coating on a Mo-9Si-8B alloy was successfully demonstrated up to 300 hrs at 1200 °C. Figure 2 and Figure 3 confirm the exclusively diffusion controlled parabolic growth rate of the thermally grown SiO<sub>2</sub> layer on silicon which has been already studied in detail for other substrate materials [24]. XRD scans confirm that the TGO forming here is cristobalite which is in accordance with most findings on silica formation on SiC and pure Si, although the temperatures for cristobalite formation given in the phase diagram under equilibrium conditions are higher [24, 25]. In our previous work on HfO<sub>2</sub>-doped and pure silicon coatings on SiC substrates we could confirm that a TGO consisting of cristobalite at about the same testing temperatures of 1250 °C forms [24]. This is consistent with findings of [26] where potential reasons for favored cristobalite formation at lower temperatures are discussed in detail.

The TGO growth rate found in the present work is in the same order as the one for PVD silicon coatings on SiC substrates, although the oxidation temperature was 50 °C higher there [24]. This implies that the Mo-bases substrate does not influence the oxidation kinetics of this coating much. The SiO<sub>2</sub> polymorph cristobalite undergoes a high/low temperature phase transitions with a CTE difference of about  $7.2 \cdot 10^{-6} \text{ K}^{-1}$  and a volume change of approximately 2.8%. This transition causes potentially tension between the SiO<sub>2</sub> layer and the non-oxidized Si-coating [24, 25, 27]. But since there was no severe oxide spallation or cracking of the TGO detected after the 300 hrs testing applied here, the coating provides great potential for prolonged oxidation protection of Mo-based alloys. Interestingly, the growth of the silica starts by forming bubbles on top of the surface. After an incubation period of 30 minutes where no bubbles form at 1200 °C, they are already present after 120 minutes of oxidation, see Figure 4. A dense and continuous TGO layer evolves as well, most likely in parallel to the formation of bubbles. Silica bubbles were not observed for the same PVD silicon coating applied on SiC substrates [24]. The bubbles do not seem to grow or increase in number, but stay nearly constant and unchanged over the entire annealing time up to 300 hrs. The silica grows continuously underneath the bubbles which do not change the local oxidation behavior substantially. This leads to the conclusion that some sort of gaseous species might form during the initial SiO<sub>2</sub> formation which initiate the bubble formation. Since the bubbly structure appears on a TZM substrate as well as on the Mo-9Si-8B alloy, boron can most likely be excluded and molybdenum or the volatile MoO<sub>3</sub> is suspected to be trapped in these bubbles. MoO<sub>3</sub> forms and volatilizes already at temperatures around 650 °C [8]. After the growth of both, the dense TGO and the interdiffusion zone, no MoO<sub>3</sub> seems to be able to move to the surface. Therefore, it is likely that small amounts of MoO<sub>3</sub> diffuse through the silicon coating onto the surface. The formation of a dense and continuous TGO layer is already completed after 5 hrs at 1200 °C. The TEM-EDS in Figure 5 provides at least some hints pointing towards molybdenum causing the initial formation of the silica bubbles.

Figure 6 indicates that the amount of  $\text{MoO}_3$  reaching the surface seems to be quite small since no internal substrate oxidation can be found after 100 hrs at 800 °C. To the best knowledge of the authors, the effect of an initially bubbly silica formation on a silicon coating has not been published so far. More detailed research has to be conducted in the near future to give more insight into the formation mechanism of the bubbles.

In the initial stages of oxidation the columnar structure of the silicon coating gets dense by rapid formation of silica along the inter-columnar gaps. This densification seals the gaps and prevents further inward diffusion of oxygen since all gaps are filled by silica which possesses a rather low oxygen diffusivity. It is possible that those early stages of oxygen inward diffusion, silica formation in the inter-columnar gaps, transient formation of (volatile) Mo-oxides and formation of silica bubbles are interconnected which is the topic of ongoing studies. But since the Si-coating can protect the Mo-9Si-8B substrate successfully from pest-oxidation after 100 hrs at 800 °C, the process of Mo-oxide volatilization might even start at more elevated temperatures drastically.

#### **4.2. Interdiffusion of silicon and molybdenum in different atmospheres**

The interdiffusion of silicon and molybdenum is widely investigated and understood in atmospheres that do not contain oxygen. In this case, silicon diffuses much faster into molybdenum than vice versa to form the phases  $\text{MoSi}_2$ ,  $\text{Mo}_5\text{Si}_3$  and lastly  $\text{Mo}_3\text{Si}$ .  $\text{MoSi}_2$  is thereby the most dominant phase followed by  $\text{Mo}_5\text{Si}_3$ .  $\text{Mo}_3\text{Si}$  occurs later as a thin layer directly on the molybdenum<sup>[12, 28-31]</sup>. In the present investigation, silicon coated TZM follows the same pattern when heat treated under vacuum, seen in Figure 10 and 11. The phase diagram of Mo-Si confirms that all three phases are possible to evolve at temperatures around 1200 °C. The study of Yoon et al. provides evidence that silicon is not able to adhere over longer annealing times to the Mo-silicide phases due to the large mismatch of the CTE

(Si:  $3.8 \cdot 10^{-6} \text{ K}^{-1}$ , MoSi<sub>2</sub>:  $9.5 \cdot 10^{-6} \text{ K}^{-1}$ )<sup>[32, 33]</sup>. In contrast to the scenario under vacuum described above, under oxygen containing atmosphere such as lab air the silicon coating on the TZM substrate behaves differently in the present study. In this case only the Mo<sub>3</sub>Si phase forms predominantly by growing into the TZM substrate, seen in Figure 10 and 11. The CTE of Mo<sub>3</sub>Si is about  $6.03 \cdot 10^{-6} \text{ K}^{-1}$ <sup>[34]</sup> which fits better to both the CTE of Mo-based alloys, silicon and silica.

Oxygen has been detected in the EDS line scan in substantial amounts in this phase. Since there is no evidence of a second phase forming other than MoSi<sub>3</sub>, the oxygen seems to be dissolved in this phase. The study also shows that the IDZ of MoSi<sub>3</sub> increases in thickness with time (Figure 8) in air. Yoon et al. describe that the Mo<sub>3</sub>Si phase grows into the Mo substrate rather than forming in the contact zone between Si and Mo. The same has been found here, i.e. formation of Mo<sub>3</sub>Si by mostly inward diffusion of silicon and formation of the phase within the former Mo-alloy, see Figure 7. Silicon is in this case the faster diffusing species as seen before in the vacuum annealing, too<sup>[35]</sup>. This is in good agreement with literature data clearly indicating that silicon is the more mobile element in all relevant Mo-Si phases due to the much higher defect concentration within the Si-sublattices<sup>[23]</sup>. A few studies aimed already at explaining the influence of oxygen on the interdiffusion between those two elements<sup>[28, 32]</sup>. Although none of the studies found the total suppression of MoSi<sub>2</sub> and Mo<sub>5</sub>Si<sub>3</sub> as demonstrated here, the explanation given there seem to hold for the present case as well. Yoon et al. concluded that the MoSi<sub>2</sub> growth rate and activation energy is heavily influenced by impurities like oxygen<sup>[32]</sup>. The growth rate decreases in an oxygen containing atmosphere which is in good agreement with the results found in this study. The present findings clearly show that no other phase than Mo<sub>3</sub>Si forms in oxygen containing atmosphere. Moreover, it dissolves substantial amounts of oxygen since there is no known phase being constituted by all the three elements Mo, Si, and O. It could be possible that oxygen might support the formation of the Mo<sub>3</sub>Si phase rather than the Si-richer Mo-silicides. How oxygen hinders the

silicon to diffuse further into molybdenum and, thereby impeding the development of silicon richer Mo-silicide could not be finally clarified within this study. But this phenomenon can also be found in Rastogi et al. [28]. There  $\text{SiO}_2$  formed at the silicon/molybdenum interface hinders the formation of silicides. In this study no  $\text{SiO}_2$  could be found below the Si-coating until now, which confirms the excellent oxidation protection of this PVD layer for Mo-based alloys.

## 5. Conclusion

In this study, a simple coating with pure Si has been successfully applied as single layer for oxidation protection by magnetron sputtering on Mo-based alloys for the first time. The coating was able to protect the Mo-9Si-8B alloy until 300 hrs of isothermal exposure at 1200 °C in lab air due to the development of a dense thermally grown silica scale on top. The protective Si-coating showed excellent adhesion on the Mo-9Si-8B substrate during prolonged oxidation. In the initial phase of oxidation, the  $\text{SiO}_2$  formed a bubbly structure. The silica bubbles did not change with time while the dense and slowly growing TGO formed underneath and thickened with time. At intermediate temperatures of 800 °C the pest-oxidation could be successfully suppressed by the Si-coating up to 100 hrs.

An interdiffusion zone consisting exclusively of the  $\text{Mo}_3\text{Si}$  phase has been formed during annealing in air by silicon inward diffusion into the Mo-based alloy. This phase contains substantial amounts of oxygen. During 300 hrs testing at 1200°C, this slow growing interdiffusion zone possess a varying thickness in the order of 1 to 2  $\mu\text{m}$ . Testing in vacuum showed the formation of an interdiffusion zone being about 8  $\mu\text{m}$  thick and containing the  $\text{MoSi}_2$  and the  $\text{Mo}_5\text{Si}_3$  phases where no oxygen has been detected. It seems to be reasonable that oxygen containing atmospheres favor the formation of  $\text{Mo}_3\text{Si}$  while suppressing the  $\text{MoSi}_2$  and  $\text{Mo}_5\text{Si}_3$  phases.

## Acknowledgements

This work was conducted under the financial support of Deutsche Forschungsgemeinschaft (DFG) within the framework of grants no. Schu1372/7-1 and HE 1872/33-1 which is gratefully acknowledged. For the scientific and technical support at the German Aerospace Centre the authors thank V. Leisner, P. Bauer, A. Handwerk, P. Herzog and F. Kreps.

## Uncategorized References

- [1] J.H. Perepezko, *Science* 326(5956) (2009) 1068-9.
- [2] A. Lange, R. Braun, *Corrosion Science* 84 (2014) 74-84.
- [3] M.R. Middlemas, J.K. Cochran, *JOM* 62(10) (2010) 20-24.
- [4] J.H. Perepezko, *International Journal of Refractory Metals and Hard Materials* 71 (2018) 246-254.
- [5] M.A. Azim, B. Gorr, H.J. Christ, O. Lenchuk, K. Albe, D. Schliephake, M. Heilmaier, *Intermetallics* 90 (2017) 103-112.
- [6] D. Schliephake, A. Kauffmann, X. Cong, C. Gombola, M. Azim, B. Gorr, H.-J. Christ, M. Heilmaier, *Intermetallics* 104 (2019) 133-142.
- [7] S. Burk, B. Gorr, H.-J. Christ, D. Schliephake, M. Heilmaier, C. Hochmuth, U. Glatzel, *Scripta Materialia* 66(5) (2012) 223-226.
- [8] D. Schliephake, C. Gombola, A. Kauffmann, M. Heilmaier, J.H. Perepezko, *Oxidation of Metals* 88(3-4) (2017) 267-277.
- [9] M.A. Azim, D. Schliephake, C. Hochmuth, B. Gorr, H.-J. Christ, U. Glatzel, M.J.J. Heilmaier, *67(11)* (2015) 2621-2628.
- [10] J.H. Perepezko, T.A. Sossaman, M. Taylor, *Journal of Thermal Spray Technology* 26(5) (2017) 929-940.
- [11] S. Majumdar, *Applied Surface Science* 414 (2017) 18-24.
- [12] S. Majumdar, I. Sharma, I. Samajdar, P. Bhargava, *Journal of The Electrochemical Society* 155(12) (2008) D734.
- [13] K. Choi, W. Yang, K.-H. Baik, Y. Kim, S. Lee, J.S. Park, *Oxidation of Metals* 92(5-6) (2019) 423-437.
- [14] A. Lange, R. Braun, M. Heilmaier, *Intermetallics* 48 (2014) 19-27.
- [15] A. Lange, R. Braun, U. Schulz, *Materials at High Temperatures* 35(1-3) (2017) 195-203.
- [16] K.N. Lee, *Ceramic matrix composites: materials, modeling and technology* (2014) 430-451.
- [17] B.T. Richards, H.N.G. Wadley, *Journal of the European Ceramic Society* 34(12) (2014) 3069-3083.
- [18] W.D. Sylwestrowicz, *Philosophical Magazine* 7(83) (1962) 1825-1845.
- [19] D. Zhu, Development and Performance Evaluations of HfO<sub>2</sub>-Si and Rare Earth-Si Based Environmental Barrier Bond Coat Systems for SiC/SiC Ceramic Matrix Composites, 41st International Conference on Metallurgical Coatings and Thin Films San Diego, (2014).
- [20] S. Obert, A. Kauffmann, M. Heilmaier, *Acta Materialia* 184 (2020) 132-142.
- [21] M. Krüger, S. Franz, H. Saage, M. Heilmaier, J.H. Schneibel, P. Jéhanno, M. Böning, H. Kestler, *Intermetallics* 16(7) (2008) 933-941.

- [22] R. Sakidja, J. Park, J. Hamann, J. Perepezko, *Scripta materialia* 53(6) (2005) 723-728.
- [23] S. Prasad, A. Paul, *Intermetallics* 19(8) (2011) 1191-1200.
- [24] R. Anton, V. Leisner, P. Watermeyer, M. Engstler, U. Schulz, *Acta Materialia* 183 (2020) 471-483.
- [25] B.T. Richards, S. Sehr, F. de Franqueville, M.R. Begley, H.N.G. Wadley, *Acta Materialia* 103 (2016) 448-460.
- [26] E.J. Opila, *Journal of the American Ceramic Society* 77(3) (1994) 730-736.
- [27] H. Salmang, H. Scholze, R. Telle, *Keramik*, Springer 1982.
- [28] R.S. Rastogi, V.D. Vankar, K.L. Chopra, *Thin Solid Films* 213(1) (1992) 45-54.
- [29] J.-K. Yoon, J.-Y. Byun, G.-H. Kim, J.-S. Kim, C.-S. Choi, *Thin solid films* 405(1-2) (2002) 170-178.
- [30] M. Salamon, A. Strohm, T. Voss, P. Laitinen, I. Riihimäki, S. Divinski, W. Frank, J. Räisänen, H. Mehrer, *Philosophical Magazine* 84(8) (2006) 737-756.
- [31] J.-Y. Byun, J.-K. Yoon, G.-H. Kim, J.-S. Kim, C.-S.J.S.m. Choi, 46(7) (2002) 537-542.
- [32] J.K. Yoon, J.Y. Byun, G.H. Kim, J.S. Kim, C.S. Choi, *Surf Coat Tech* 155(1) (2002) 85-95.
- [33] M. Rice, K. Sarma, *Journal of The Electrochemical Society* 128(6) (1981) 1368-1373.
- [34] J.H. Schneibel, C.T. Liu, D.S. Easton, C.A. Carmichael, *Materials Science and Engineering: A* 261(1) (1999) 78-83.
- [35] J.K. Yoon, J.K. Lee, K.H. Lee, J.Y. Byun, G.H. Kim, K.T. Hong, *Intermetallics* 11(7) (2003) 687-696.

## Table of Content

Mo-based alloys are attractive high temperature structural materials for future applications in gas turbines. A simple silicon coating has been applied for oxidation protection by magnetron sputtering for the first time. The coating was able to protect the Mo-9Si-8B alloy until 300 hrs of isothermal exposure at 1200 °C in lab air by formation a dense thermally grown silica scale on top.

**oxidation behavior**

Ronja Anton\*, Nadine Laska, Uwe Schulz, Susanne Obert, Martin Heilmaier

**Magnetron sputtered silicon coatings as oxidation protection for Mo-based alloys**