Ceramic oxidation protection coatings for refractory alloys from filler-loaded preceramic polymers: The role of particle size and volume fraction of particulate fillers

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Abstract. Oxidation protection coatings on the base of perhydridopolysilazane (PHPS) polymer and Si/B filler materials were developed to prevent Mo-based alloys against oxidation at 800 °C. Within this work the influence of the particle size and the volume fraction of particulate fillers on the oxidation protective effect of the coatings was investigated. Double and triple coatings were applied in order to determine the effect of layer thickness on the oxidation resistance properties.

1 Introduction

In stationary gas turbines and aircraft engines, nickel-based superalloys are used as turbine blades at high temperatures. However, these superalloys (in monocry stalline and coated forms) have reached the point of maximum application temperatures at 1150 °C, which results in a homologues temperature of around 800 °C [1]. Potential materials for the high-pressure turbine application are molybdenum alloys, which due to their high melting temperature of over 2000 °C and high temperature mechanical properties represent an excellent alternative to substitute nickel-based alloys [2, 3]. Nevertheless, the problem of massive oxidation arises for fine-grained molybdenum alloys in the temperature range from 750 °C to 900 °C [4]. For this reason, it is necessary to apply a protective barrier coating against oxidation on the surface of most Mo-based materials.

Polymer-derived ceramics provide a cost-effective and perspective method of coating applications. For an effective Mo-alloy protection a coating system based on pre-ceramic polymer filled with ceramic and/or metal particles is considered. A polymer precursor forms a thermoset during a crosslinking process, which in a subsequent temperature treatment step – the pyrolysis – is converted into an amorphous ceramic caused by a polymer-to-ceramic transformation process. [5]. The fillers serve three main functions: they increase a coating thickness compared to unfilled coating systems; they reduce the shrinkage of the coating during polymer-to-ceramic transformation and they form new phases through reactions with the pre-ceramic polymer and the surrounding atmosphere as working medium that intend to compensate a possible volume change due to oxidative processes on the coated surfaces [6].

In this work coatings with a perhydridopolysilazane (PHPS) polymer based on Si and N in their molecular arrangement were produced as protective systems for Mo-based alloys. Powders of Si and B were used as filler materials, which, due to their strong chemical affinity to oxygen, may form SiO2-B2O3 glass phases with a self-healing effect and have an average or a large increase in volume [7, 8].
Determining corresponding oxidation kinetics, the specific surface area of the particles plays a decisive role that can be controlled by the particle size and the volume fraction of fillers. Thus, in the present work coatings with fillers of various sizes were developed, and the effect of the particle size and their volume fraction on the oxidation kinetics of coating systems was investigated.

2 Experimental procedure

For the coating system a commercially available perhydridopolysilazane PHPS NN 120-20 (Clariant Advanced Materials GmbH, Sulzbach, Germany) was used. Boron amorphous powder with a particle size of 1-5 μm (Chempur, Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe, Germany) and silicon crystalline powders of 1-5 μm and 5-17 μm in particle size (Thermo Fisher GmbH, Kandel, Germany) were received from commercial supplier in high purity quality. A silicon powder with the specific particle size of 4-12 μm was received by a powder metallurgical processing route: -100 mesh silicon was planetary ball milled for 0.5 h at 200 rpm. The particle size distribution of the modified and unmodified particles was determined using a laser diffraction analyser (Mastersizer 2000, Malvern Instruments), which is suitable for the non-destructive analysis of wet and dry dispersed particles with a size ranging from 0.02-2000 μm. The particle size distribution of filler materials is presented in figure 1. The main important properties of the filler materials and their schematic sample codes are summarized in table 1.

![Particle size distribution](image)

**Figure 1.** Silicon particle size distribution.

Preceramic slurries for the coating systems were mixed in a specific precursor-to-filler volume ratio: 72 PHPS + 17.5 Si + 10.5 B and 65 PHPS + 22 Si + 13 B, all numbers in vol. %. Powders were introduced into the precursor solution (20 wt. % of PHPS in dibutyl ether) by vigorous stirring under air. The coating systems were developed on the base of our previous work and the preparation rout is described in detail in [7, 8]. Also, the process of the PHPS polymer/(Si+B) filled precursor-to-ceramic conversion, the coatings’ phase composition and the microstructure are reviewed in the references above. The coating consists of Si and B particles surrounded by the polymer derived (PDC) matrix phase, SiON, along the filler grains and in the vicinity of a SiO2 glassy phase [7]. The aim of this work is to investigate an
influence of the particle size and volume fraction of filler materials on the oxidation kinetics of the coatings.

### Table 1. Filler properties and samples codes.

| Filler | Producer | Purity, % | Particle size, (μm) | Density, (g/cm³) |
|--------|----------|-----------|---------------------|-----------------|
| I. Si  | Silicon Powder, crystalline, APS 1-5 μm, Thermo Fisher GmbH | 99.9 | 2.9-5.6 | 2.3 |
| II. Si | Silicon Powder, crystalline, -100 mesh, Thermo Fisher GmbH | 99.9 | 4.0-12.4 |
| III. Si| Silicon Powder, crystalline, -325 mesh, Thermo Fisher GmbH | 99.5 | 5.0-16.3 |
| B      | Chempur GmbH, amorphous | 98.0 | 2.3-8.2 | 2.1 |

For applying the coatings a dip coating process was carried out with a withdrawal speed of 3 mm/s and a sample holding time in the coating system of 10 s. The coatings were applied on the previously prepared samples of a plain Mo alloy (E. WAGENER GmbH, Heimsheim, Germany, 99.95 % purity) and arc melted Mo-14Hf-23B and Mo-14.8Zr-26B (in at. %) alloys. Processing of Mo-14Hf-23B and Mo-14.8Zr-26B is carefully described elsewhere [8]. It was found that the coating process must be carried out on the surface of Mo-basis alloys repeatedly, since all Mo is vaporized through the areas where the substrate was fixed on the holder for dip coating [8]. Thus, in this work double and triple coating was applied to Mo-basis alloys. The coated samples were heated to 110 °C with a slope of 2 K/min in air for 1 – 1.5 h to allow crosslinking. Pyrolysis was conducted in nitrogen atmosphere in a tube furnace (HTRRH 70-600/18, Fa. Gero Hochtemperaturöfen GmbH & Co. KG, Neuhausen) for 1 h at 1000 °C; heating and cooling rates were 3 K/min.

To produce thick coating layers with the dip coating method an important issue for filler loaded precursor systems is a uniform dispersion of solid phases in the fluid medium, aimed to avoid sedimentation [9]. Another issue is, that the filler loaded systems should have a low viscosity under high withdrawal speed at the beginning of the dip coating process, and a high viscosity after the discontinuation of the withdrawal stresses. In this study a viscosity of the coating slurries was measured using a rotational viscometer MCR 301 (Anton Paar Germany GmbH, Ostfildern-Scharnhausen/Germany) in a plate-to-plate configuration with a gap size of 1 mm. The measurement was carried out at room temperature a variation of the shear rate from $10^1$ s⁻¹ to $10^3$ s⁻¹. In accordance to the plate-to-plate measuring/sensor system the share rate values correspond to the withdrawal speed during dip coating [10]. The correlation between the shear rate and the withdrawal speed is represented by equation (1):

$$\dot{\gamma}_a = \frac{2}{3} \frac{mm}{m} \cdot U,$$

(1)

where $\dot{\gamma}_a$ is the average shear rate und $U$ is the withdrawal speed.

In accordance with the Landau-Levich theory the thickness of the coating, $h_0$, could be estimated by equation (2) [11]:

$$h_0 = c_1 \sqrt{\frac{\eta U}{\rho g}},$$

(2)

where $c_1$ is a proportionality constant, $\eta$ is the viscosity of the suspension, $\rho$ is the density of the suspension and $g$ is the gravitational acceleration.

The coating thickness is proportional to the viscosity of the coating system and the withdrawal speed and inversely proportional to the density. Thus, changing the withdrawal speed and the viscosity of the coating slurry the thickness of the coating can be adjusted. These relationships relate to an idealized continuous process, in which a sample is hoisting up at a constant speed. It means that in the case of discontinuous operation, the coefficient in the formula must be adapted to the respective system.
Moreover, the Landau-Levich theory requires a purely Newtonian behaviour, i.e., no shear thinning or thickening of the slurry. The particle-filled coating system cannot be directly regarded to this. Nevertheless, M. Günthner et al. [12] use this theory to explain the thickness of precursor/BN composite coatings. In our work, we have considered the possibility of Landau-Levich theory application for previous calculations of the coating thicknesses regarding developed coating systems. The value of the layer thickness relates to the layer after being withdrawn immediately from the slurry. The reason for this is that the suspension continuously flows from the substrate until it is completely dry, and the resulting coating shrinks during pyrolysis due to the polymer component.

The microstructure characterization and phase analysis of compact samples with the coating composition, prepared for comparison, were carried out with an X-ray diffractometer (XPERT PRO PANalytical, Malvern Panalytical GmbH) using Co-Kα radiation and scanning electron microscopy (HR-FESEM, Zeiss Merlin equipped with an EDS detector, Carl Zeiss Microscopy GmbH, Jena, Germany; and FEI DualBeam Scios, FEI Company, Hillsboro, USA).

Cyclic oxidation tests of coated samples were performed in a convection furnace (Model L9/S17, Nabertherm, Lilienthal) at 800 °C in air. Interval withdrawal of samples for characterization was carried out in 20 h steps up to 100 h. The specific mass change of the samples was measured using an analytical balance with an accuracy of 0.0001 g.

3 Results and discussion

3.1 Viscosity measurements and determination of the coating thickness.

Important for the coating process is the rheological behavior of the pre-ceramic slurries. In the first stage of our investigation viscosity measurements of the 72 PHPS + 17.5 Si + 10.5 B, vol. %, coating system with different particle size of silicon were carried out, figure 2. The measurements were conducted in air soon after preparing the coating slurries, because they tend to crosslink even at room temperature and their viscosity may increase.

![Figure 2. Viscosity versus shear rate of the filler loaded pre-ceramic coating slurry with Si fillers of different particle sizes.](image)

All coating slurries independent from their silicon particle size demonstrate a shear thinning behaviour, owning a low viscosity under high shear rates, and a high viscosity after the discontinuation of the shear stress. Such kind of behaviour provides an opportunity of dip coating application on all type of substrate materials: a low viscosity of the slurry while dipping the sample, and a high viscosity after withdrawing the sample for coating deposition.

Retaining a constant volume fraction of particles in the slurry while reducing the silicon particle size leads to an increase of the particle number in the coating system. A higher number of smaller particles
results in more particle-particle interaction processes and an increased resistance to flow. Therefore, the coating slurry with Si I (1-5 μm) particles demonstrates higher viscosity compared to slurry with Si II (4-12 μm) at low shear rates. An exception is the coating slurry based on Si III (5-16 μm) particles, which has a higher viscosity than Si I and Si II. This can be explained by a broader particle size distribution of the silicon powder and a partial obstruction to shear by some larger particles. This may be evidenced by the higher viscosity of this coating slurry compared to the other two at both, low and high shear rates.

The particle-particle interactions are relatively weak and broke down with an increase of the shear rate. Thus, the particles size effect became less visible at high shear rates for all coating slurries.

Using respective viscosity values at definite shear rates, the expectable coating thickness was calculated according to equation (2), considering a correlation between the shear rate and the withdrawal speed represented in equation (1). The calculated coating thickness for the three coating systems at a given withdrawal speed of 3 mm/s is summarized in table 2.

| Coating thickness in μm | System: 72PHPS+17.5Si+10.5B, vol. % |
|------------------------|--------------------------------------|
| I. Si                  | II. Si                               | III. Si                             |
| 32.4 μm                | 29.5 μm                              | 35.8 μm                             |

In accordance with calculations, the theoretical coating thickness should be in the range from 30-35 μm. As it was mentioned above, these values respond to the coating layer direct after withdrawing the sample from the slurry and excluding the shrinkage of the coating caused by crosslinking and pyrolysis. Thus, the resulting coating thickness is expected to be lower.

The coating deposition on the surface of plain Mo and Mo-14Hf-23B and Mo-14.8Zr-26B alloys was carried out according to the distinguished procedure described in section 2. Before deposition, the alloy samples were ground with SiC paper FEPA P1200 (17.3-19.3 μm) and cleaned in an acetone (80 vol. %) / ethanol (20 vol. %) mixture by ultrasonic treatment, and subsequently dried. The double and triple coating layers were achieved by one and two times overcasting the first layer followed by crosslinking and pyrolysis after each step. The microstructures of coated Mo-alloy samples are presented in the figure 3.

![Figure 3. Microstructure of double (a) and triple (b) 72 PHPS + 17.5 Si +10.5 B, vol. %, coatings on the surface of Mo-alloys.]
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The resulting coating composition and the phase analysis are detailed described elsewhere [7, 8]. According to macro structural studies, the coating layers were homogeneous across the entire surface of the samples and did not have any phase segregation. However, some pores in the inner layers of the coatings were obtained using Si II and Si III fillers as imaged by SEM. This may be caused by in the broader particle size distribution of the silicon powder in these types of fillers that might interfere with the package density of the particles. Nevertheless, no through pores or pores entering the outer protective layer were formed. In turn, the coatings with Si I filler was homogeneous across the sample’s cross section and any pores were detected between coating layers. It must be mentioned, that the overcoating of the first coating layer leads to an increase in thickness of the second and the third layer compared to the first layer. This may be caused by a purity change of the sample’s surface and an increase of the surface roughness.

The thickness of the coatings ranged from 50 µm to 54 µm for double layers and from 70 µm to 79 µm for triple layers. In conformity with theoretically calculated coating thicknesses with the Landau-Levich theory, these values are somewhat lower in compared to 30-35 µm for a single layer; this was expected due to shrinkage processes. Considering the lack of prediction of coating shrinkage during pyrolysis, the Landau-Levich theory may be used to estimate the coatings thickness.

3.2 Oxidation resistance of the PDC coatings.
Aim of this work is the oxidation resistance study of coatings with respect to the role of particle size and volume fraction of particulate. As the first step the oxidation protection properties of the double and triple coatings were examined on Mo-alloys. The oxidation investigations were conducted at 800 °C, the harshest temperature for Mo-based alloys because of the pesting phenomenon, which means the formation of a volatile MoO₃ phase [13]. The oxidation curves of double and triple coated Mo-samples are presented in figure 4 (a).

![Figure 4](image_url)

**Figure 4.** Oxidation curves at 800 °C in air (up to 100 h) of double and triple coated Mo- (a) and Mo-14Hf-23B and Mo-14.8Zr-26B (b) samples with coatings of the composition 72 PHPS + 17.5 Si + 10.5 B; numbers in vol. %.

Double coated samples show a significant mass loss already after 20 h of high temperature (800 °C) exposure to air with the plain Mo samples. Up to 40 h of oxidation the samples lost their mass in a catastrophic course. The destruction of the coating layers is observed starting at 20 h and the further mass loss is caused by evaporation of MoO₃ through damaged coating areas.

The triple coatings demonstrate a more stable behavior up to 20 h, but it cannot be considered as a protective coating. For the coatings with Si I and Si III for the first 20 h a slight increase in mass was observed. This might be assumed as a formation of the SiO₂-B₂O₃ passivation layer as a result of B and
Si oxidation with oxygen from air. However, after 20 h of oxidation the mass loss indicates the beginning of MoO$_3$ evaporation. The highest mass loss is identified for the samples coated with Si I in comparison to samples with Si II and Si III. It is initially surprising, because smaller particulate fillers should provide a higher specific surface area and as a result a higher reactivity of Si with oxygen to form a protective glassy layer. Evidently, the viscosity of SiO$_2$-B$_2$O$_3$ coating layer at the initial stage of oxidation is still too high to prevent from oxygen penetration into the metal substrate [14]. The formation and evaporation of MoO$_3$ destroys the glassy layer and provokes a further penetration of O$_2$ into the matrix that repeats the process.

For the coatings on Mo-14Hf-23B and Mo-14.8Zr-26B surfaces the system with Si III was applied. The cyclic oxidation curves of double and triple coated and uncoated samples are presented in figure 4 (b). As can be seen in the graph, uncoated Mo-14Hf-23B and Mo-14.8Zr-26B alloys show dramatic mass losses when the peak temperature (800 °C) is reached. The more detailed description of the cyclic oxidation behaviour of Mo-14Hf-23B and Mo-14.8Zr-26B at 800 °C is described elsewhere [8]. The oxidation proceeds due to the formation of MoO$_2$ and MoO$_3$ oxides and the evaporation of the last one. As a result of MoO$_3$ evaporation Hf(MoO$_2$)$_2$ and Zr(MoO$_2$)$_2$ ternary oxides are detected by XRD analysis on the surface of the samples. A boron-containing oxide was not found by XRD.

Nevertheless, the triple coated Mo-14Hf-23B and Mo-14.8Zr-26B alloys did not show any mass change after 40 h of exposure up to 100 h. Up to 20 h a slight mass increase in these samples corresponds to the formation of a protective glassy layer. This oxidation behaviour is obviously related to the possibility of Mo-14Hf-23B and Mo-14.8Zr-26B to form B$_2$O$_3$, compared to plain Mo, which may control the viscosity of the glassy layer on the interface between coating and substrate [13]. The glassy nature of the coating was proven by EDS analysis of the triple coated Mo-14.8Zr-26B after 100 h of cyclic oxidation at 800 °C, see figure 5. It must be mentioned, that the total coating thickness was increased from 73 µm to 106 µm as a result of oxidation that, in turn, confirms the formation and growth of the SiO$_2$-B$_2$O$_3$ layer.

![Figure 5. Triple coated Mo-14.8Zr-26B sample after 100 h of cyclic oxidation in air at 800 °C.](image)

The thickness of the double coatings on Mo-14.8Zr-26B alloy was 50 µm in the initial state. Evidently, this thickness cannot protect the sample from oxidation, see figure 4 (b).

To investigate the influence of the volume fraction of particulate fillers on the oxidation behavior of the coatings slurry with an increased amount of silicon and boron was developed: 65 PHPS + 22 Si + 13 B, vol. %. To obtain a 70 µm to 90 µm thick coating that was found to be effective against oxidation using the previous slurry, a double coating was applied to simplify the procedure. The calculations of the expected coating thickness were conducted by equation (2) considering the modified density and viscosity of the modified slurry. The triple coatings were as well applied to the surface of plain Mo and Mo-14.8Zr-26B alloys; these thickness reached 150-155 µm.

The mass change curves of the double and triple coating with 65 PHPS + 22 Si + 13 B, vol. % slurry samples are presented in figure 6. It is evident that an increase of the volume fraction of fillers in the
slurry and an enhancement of the coating thickness do not have a profitable effect on the improvement of oxidation resistive properties of plain Mo: a significant mass loss is observed for all samples, see figure 6 (a). The performance of the triple layered coating, however, is higher than that of the double layered coating, see figure 6 (b).

![Figure 6](image)

**Figure 6.** Oxidation curves of double and triple coated Mo- (a) and Mo-14Hf-23B and Mo-14.8Zr-26B (b) samples with 65 PHPS + 22 Si + 13 B, vol. %.

The triple coating with the thickness of 153 µm shows a minor mass loss after 20 h of oxidation. However, this mass loss is not caused by the MoO3 evaporation, but by some detachment of the coating layer, as found after oxidation treatment and sample revision. Obviously, the thickness of the coating and the number of coating layers play a significant role for the protective function. Nevertheless, increasing the coating thickness above 90 µm does not improve the oxidation resistance of the alloys; the effect of coating spalling is currently under investigation.

### 4 Conclusions

Oxidation protection coating systems developed in this work were proven to be appropriate for improving the oxidation resistance of Mo-14Hf-23B and Mo-14.8Zr-26B alloys at 800 °C. These alloys, in contrast to plain Mo alloy, can generate a B2O3 phase during initial oxidation, while the oxygen-trapping coating systems slow down the oxygen intake into the alloy. This may provide time for the formation of a low-viscosity glassy layer on the interface between coating and substrate, which, in turn, provides a protection against oxidation in the initial stage of high temperature exposure.

An increase of the volume fraction of particulate Si and B fillers in the slurry lead to an increase of the coating thickness; this showed a negative influence on the oxidation resistance on coatings because of undesired spalling effects.

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