An ultra-high temperature Mo-Si-B based coating for oxidation protection of Nb_{SS}/Nb₅Si₃ composites

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Abstract: A Mo-Si-B based coating was prepared on a Nb_{SS}/Nb₅Si₃ composite by a two-step process consisting of the initial deposition of Mo followed by pack cementation co-deposition of Si and B. After a conditioning treatment, an aluminoborosilicate layer fully covered the sample. Following oxidation at 1300°C for 24 h, the coated sample demonstrated a weight loss of about 0.55 mg/cm² and the uncoated sample exhibited catastrophic oxidation with a weight gain of 87.6 mg/cm². These results demonstrate that the Mo-Si-B based coating can enable the use of the Nb_{SS}/Nb₅Si₃ composites at temperature up to 1300 °C in an oxidizing environment.

Keywords: Intermetallics; Metal Coatings; EPMA; SEM; Oxidation

1. Introduction

The Nb-based alloys have attracted significant research interest as a promising candidate material for high temperature applications in aeronautical and aerospace fields because of their excellent mechanical properties at high temperatures [1-3]. However, the poor oxidation resistance of these alloys at high temperatures in an oxidizing environment causes catastrophic degradation to the material [2]. While the oxidation resistance of Nb-Si based alloys has been improved by alloying with elements such as Al, Cr, Hf, Sn, B and Ge, the additions often lead to a deterioration of the mechanical properties [2, 4-6]. Therefore, the application of a coating is considered an effective way to address the requirement of an enhanced resistance to environmental attack in high-strength Nb-based alloys.

A series of oxidation-resistant coatings have been developed in previous studies

to provide protection for Nb-based alloys. Aluminide and silicide coatings have been investigated extensively due to the oxidation protection of the Al_2O_3 and SiO_2 scales that form during high temperature exposure. For example, Hayashi et. al. have developed an exclusive Al_2O_3 scale by a diffusion aluminizing process on a Nb-based alloy [7]. Similarly, Knittel et al. have studied $(\text{TiNbXCr})_7\text{Si}_6$ (with $\text{X}=\text{Fe}, \text{Co}$ and Ni) coatings by pack cementation on a Nb-based alloy to form a protective scale at 1100°C and 1200°C [8]. Furthermore, silicides that are modified with elements such as Al, Cr, Ge and Y have also been applied on Nb-based alloys by pack cementation techniques for oxidation protection at 1250°C in air [9-12]. However, none of the reported coatings applied on Nb-based alloys have been demonstrated to successfully survive at temperatures above 1250°C .

On the other hand, molybdenum silicides have drawn a great attention as promising materials for high temperature oxidation resistant coating because of their high melting point and excellent high temperature oxidation resistance [13-15]. Studies on Mo-Si-B alloys show that oxidation resistance is achieved above 900°C due to the formation of a passive oxidation layer of borosilica [16, 17]. Furthermore, recent advances in developing coatings for Mo base alloys have been utilized to design a multilayer coating which has yielded robust oxidation resistant performance with an extended lifetime at ultra-high temperatures up to at least 1700°C [18, 19]. The Mo-Si-B coatings are applied by a pack cementation process followed by a conditioning treatment involving elevated temperature exposure in an oxidizing environment. Moreover, other research has shown that a Mo-Si-B coating can be applied via plasma spray deposition [20]. The multilayer coating structure consists of an outer aluminoborosilica layer with an underlying Mo_5Si_3 (T_1) phase layer that is saturated with boron and a subsequent layer of the Mo_5SiB_2 (T_2) phase that is in equilibrium with the substrate. The outer aluminoborosilica layer limits inward diffusion of oxygen, while the boron-saturated Mo_5Si_3 layer provides a reservoir of silicon and boron to supply the outer layer and allows for a self-healing capability. In addition, the Mo_5SiB_2 layer functions as a diffusion barrier to maintain the integrity of the coating against dissolution into the substrate. At the same time, the Mo-Si-B based

coatings have been also applied successfully on SiC/C composites, tungsten and cermets (W-HfN and Mo-ZrN) [21-23]. In this case, the coatings are developed by a two-step process consisting of the initial deposition of Mo followed by the pack cementation process. After a conditioning treatment, the coating structure consists of an outer of aluminoborosilica layer and an underlying layer of MoSi₂, which functions as the oxidation resistant layer.

Furthermore, the coefficient of thermal expansion (CTE) of Nb-Si based alloys and MoSi₂ are approximately $8.4 \times 10^{-6}/^{\circ}\text{C}$ and $8.5 \times 10^{-6}/^{\circ}\text{C}$ respectively [24]. The CTE difference between the coating and the substrate at any temperature should be less than 10%, which is desirable for reducing and potentially eliminating vertical crack formation. Therefore, a Mo-Si-B based coating is an attractive candidate to protect Nb-based alloy from high-temperature oxidation and is the focus of this paper. In order to evaluate the performance of the Mo-Si-B based coating, the microstructure and oxidation resistance of on coated and uncoated Nb_{SS}/Nb₅Si₃ composite sample were investigated.

2. Materials and methods

The Nb_{SS}/Nb₅Si₃ composite with a composition of Nb-15Si-24Ti-4Cr-2Al-2Hf (at.%) was synthesized by a liquid metal-cooled directional solidification conducted in a vertical Bridgman furnace at 1900 °C with the withdrawal rate of 600 μm/s. This composition was chosen due to the more simplistic two-phase microstructure (Nb_{SS} and Nb₅Si₃) while variations of this alloy have shown a balance of high temperature strength and oxidation resistance [5]. After the directional solidification, the bar was subsequently heat treated at 1450°C for 12 hours, which ensured the equilibrium microstructure. The microstructure of this alloy consisted of light grey Nb_{SS} and dark grey Nb₅Si₃, as shown in Fig.1.

The Mo-Si-B coatings were applied by a two-step process. The first step consisted of depositing a molybdenum layer onto the Nb_{SS}/Nb₅Si₃ composite samples (2 mm thickness and 12 mm diameter) through the decomposition of molybdenum hexacarbonyl (Mo(CO)₆). To ensure that there was a minimal amount of oxygen in the system, the quartz tube was evacuated and backfilled with argon to create an inert

environment. The furnace was then heated to a temperature of 300 °C, at which point the boat filled with carbonyl powder was inserted into the furnace next to the alumina boat with the samples. At this temperature, the carbonyl sublimates and then decomposes forming molybdenum that deposits on the Nb₅₅/Nb₅Si₃ composite samples, according to $\text{Mo(CO)}_6 \rightarrow \text{Mo} + 6(\text{CO})$ [19]. To increase the bonding strength between the substrate and Mo layer, the samples were etched in solution consisting of HCl, HNO₃, and HF for 5 min prior to the deposition of the initial Mo coating.

The second step was to deposit silicon and boron simultaneously through a pack cementation process. In the study by Rapp et. al., a B-modified silicide coating was successfully produced by using a stable TiB₂ as the B source rather than using a pure high activity B [25]. The boron activity of several borides such as SiB₂, CrB₂ and TiB₂ were reported in this study. On the other hand, the oxides of Cr could vaporize at temperatures higher than 1200 °C [26], which means that the Cr oxides would vaporize during oxidation and they would not degrade the integrity of glass coating applied on the substrate. Therefore, CrB₂ was chosen as the boride source in this study. The powder mixture used for pack cementation consisted of 33.33 wt.% Si, 1.67 wt.% CrB₂, 2.5 wt.% NaF and the remainder Al₂O₃ powder. The samples were then placed in an alumina boat and completely immersed in the powder mixture. The boat was placed in an alumina tube that was placed in a SiC element furnace. The pack cementation process was conducted at 1000°C for 25 h in an Ar environment. Further details of the coating process are described elsewhere [22].

After a conditioning treatment at 1300 °C for 2 hours in air, the coated samples were tested at 1300 °C for 24 h in a thermogravimetric analyzer (Netzsch STA 409 CD, Selb, Germany) in an environment where O₂ was introduced at 20 ml/min once the test temperature was reached to determine the in-situ weight change.

After oxidation tests, the samples were cut in half and polished. The microstructural characterization was carried out using a LEO 1530 scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) using backscattered scanning electron (BSE) modes. The X-ray diffraction (XRD) patterns were obtained from a Bruker D8 X-ray diffractometer operated with 40 kV and 40

mA (Cu K α radiation). The composition of the coatings were analyzed by an electron probe micro-analyzer (EPMA, UW-Madison Cameca SX51 electron microprobe, utilizing Probe for Windows-Enterprise software) equipped with wavelength dispersive spectroscopy (WDS).

3. Results and discussion:

3.1 Mo deposited layer

A plan view image of the molybdenum coating on the Nb₅₅/Nb₅Si₃ sample using the molybdenum hexacarbonyl deposition technique is shown in Fig. 2a. The molybdenum particles are densely packed and are approximately 2 μ m in diameter. The molybdenum layer formed is approximately 15-17 μ m thick as seen in Fig. 2b.

Fig. 3a shows the XRD pattern from the surface of the Mo-Si-B coating and reveals strong peaks for MoSi₂ and a broad diffuse maximum for amorphous silica are detected in the as-pack coating. Fig. 3b and Fig. 3c display the surface and cross-sectional BSE images respectively of the as-pack sample. The chemical composition analysis results by EPMA are presented in Table 1. The detailed view of the coating structure shown in Fig. 3c demonstrates that the coating adherence is maintained and that the Nb₅₅/Nb₅Si₃ composite microstructure is unaltered by the pack cementation coating synthesis process. Moreover, the coating is relatively dense and continuous, and no significant cracks are observed. As shown in Fig. 3b, the deposited coating is about 50 μ m thick and has a multilayer structure, consisting of a 25 μ m thick outer layer with bright contrast, a 5 μ m thick middle layer and a 20 μ m thick inner layer with grey contrast. According to the WDS analysis, the outer layer mainly consists of MoSi₂. It is noted that this layer contains 6.97 at.% O and the ratio of Si to Mo (at.%) is a little higher than 2, suggesting that this layer is comprised of SiO₂ as well as MoSi₂. Following the pack cementation coating synthesis, the Mo coating is converted into an outer layer of MoSi₂ and aluminoborosilica (as shown in Fig.3b). The formation of aluminoborosilica glass can be understood from the fact that during the pack cementation process the Al₂O₃ powder is incorporated into the borosilica. In addition, sodium originated from the NaF powder source is detected in

this layer. WDS analysis suggests that the middle layer is composed of $(\text{Nb,Ti})_5\text{SiB}_2$ (bright contrast) and borosilica (black contrast). The inner layer is confirmed to be $(\text{Nb,Ti})\text{Si}_2$. The WDS analysis results show that MoSi_2 and $(\text{Nb,Ti})\text{Si}_2$ have no solubility for boron, and boron mainly exists in the $(\text{Nb,Ti})_5\text{SiB}_2$ phase.

3.2 Conditioning treatment at 1300 °C for 2 hours

The coated sample was conditioned at 1300 °C for 2 h in air before testing in the thermogravimetric analyzer. The purpose of the conditioning process is to generate an outer continuous aluminoborosilica layer on the surface in an oxygen rich environment upon elevated temperature exposure. As shown in Fig. 4a, the surface of the conditioned coating mainly consists of an aluminoborosilica layer. In addition, some white regions are distributed in this layer. These white regions are confirmed to be MoSi_2 according to EDS analysis. After the conditioning treatment, as the sample is taken out from the furnace, some small parts of the aluminoborosilica layer flakes off from the sample during the cooling process, leading to the exposure of some MoSi_2 on the surface (as shown in Fig. 4a). The cross-sectional BSE image in Fig. 4b reveals that the conditioned coating is about 60 μm thick and has a multilayer structure, consisting of a 25 μm thick MoSi_2 layer and a 25 μm thick $(\text{Nb,Ti})_5\text{Si}_3$ layer. Again, a 5 μm thick layer consisting of $(\text{Nb,Ti})_5\text{SiB}_2$ and SiO_2 is located between the MoSi_2 and $(\text{Nb,Ti})_5\text{Si}_3$ layers. An aluminoborosilica layer with a thickness of 5 μm develops on the outermost layer of the coating. This layer could inhibit further rapid oxidation and lead to a more limited oxygen diffusion rate. It should be noted that $(\text{Nb,Ti})\text{Si}_2$ layer converts into $(\text{Nb,Ti})_5\text{Si}_3$ due to the inward diffusion of Si during the conditioning process. This transformation is beneficial to CTE matching of the different coating layers. The mismatch in coefficient of thermal expansion of different layers results in the residual thermal stresses developing in the coating, which may cause spalling upon thermal cycling.

An approximation for the magnitude of the stress on cooling can be calculated using an analysis equation for simple one dimensional elastic thermal stress. The thermal stress in the coating can be calculated by:

$$\sigma_R = E_c(\varepsilon_c - \varepsilon_s) \quad (1)$$

where σ_R is the residual stress in the coating, E_c is the Young's modulus of the coating, ε_c is the thermal strain of the coating, and ε_s is the thermal strain of the substrate [27]. The thermal strain can be also calculated by:

$$\varepsilon = \alpha \times \Delta T \quad (2)$$

where α is the coefficient thermal expansion, ΔT is the temperature range [28].

Therefore, by combining Eq. 1 and Eq. 2:

$$\sigma_R = E_c \Delta T (\alpha_c - \alpha_s) \quad (3)$$

In this study, the niobium silicide is a layer between the substrate and the oxidation resistant MoSi_2 layer. The CTE matching between layers is of crucial importance to the design of a compatible coating. As reported, the coefficient of thermal expansion of the MoSi_2 , NbSi_2 , Nb_5Si_3 and $\text{Nb}_{55}/\text{Nb}_5\text{Si}_3$ composite are $8.4 \times 10^{-6}/^\circ\text{C}$, $11.2 \times 10^{-6}/^\circ\text{C}$, $9.0 \times 10^{-6}/^\circ\text{C}$ and $8.5 \times 10^{-6}/^\circ\text{C}$ respectively [24, 29, 30]. The Young's modulus of NbSi_2 and Nb_5Si_3 are 343 GPa and 377 GPa respectively [31]. The thermal stress between NbSi_2 coating and substrate (σ_R') and the thermal stress between Nb_5Si_3 coating and substrate (σ_R) can be calculated by

$$\begin{aligned} \frac{\sigma_R'}{\sigma_R} &= \frac{E_c' \Delta T (\alpha_c' - \alpha_s')}{E_c \Delta T (\alpha_c - \alpha_s)} \\ &= \frac{(343 \times (11.2 - 8.5)) \Delta T}{(377 \times (9.0 - 8.5)) \Delta T} = 4.9 \end{aligned}$$

Therefore, the transformation of NbSi_2 to Nb_5Si_3 will decrease the CTE difference between the coating and substrate, leading to a reduction in thermal stress by a factor of 5 and a reduction in vertical crack formation which will yield enhanced mechanical compatibility.

3.3 Thermogravimetric analysis

Fig. 5 shows a thermogravimetric analysis curve of an uncoated $\text{Nb}_{55}/\text{Nb}_5\text{Si}_3$ sample and a Mo-Si-B coated sample after oxidation at 1300 °C for 24 h. The uncoated $\text{Nb}_{55}/\text{Nb}_5\text{Si}_3$ sample experiences linear oxidation with a weight gain of 87.6 mg/cm^2 . The coated $\text{Nb}_{55}/\text{Nb}_5\text{Si}_3$ sample experiences a transient oxidation stage followed by a steady state oxidation stage with a weight loss of about 0.55 mg/cm^2 , which indicates that the coated sample is protected at 1300 °C. The transient

oxidation stage in the Mo-Si-B coated sample is characterized by rapid mass loss due to volatilization of MoO_3 from the exposed surface area of MoSi_2 as shown in Fig. 4a during initial oxidation at elevated temperatures in the thermogravimetric analyzer. After the transient period, the silica generated from the oxidation of MoSi_2 develops on the sample surface. Once the SiO_2 formed due to oxidation and the aluminoborosilica formed due to the conditioning step cover the entire sample, the steady state stage of the oxidation begins.

Fig. 6 shows the appearance of the uncoated and coated $\text{Nb}_{55}/\text{Nb}_5\text{Si}_3$ samples after oxidation at 1300 °C for 24 h. As shown in Fig. 6a, the oxide scale formed on the surface of the uncoated sample exfoliates indicating catastrophic oxidation. However, the scale formed on the surface of the Mo-Si-B coated sample is dense and tightly adherent, indicating that the sample is protected upon oxidation (as shown in Fig. 6b).

To identify the phases developed on the uncoated and coated samples after oxidation at 1300 °C for 24 h, the sample surfaces were analyzed by X-ray diffraction (as shown in Fig. 7a). The main oxide formed on the uncoated sample is identified as TiNbO_7 . The XRD pattern for the coated sample shows strong peaks for MoSi_2 and a broad diffuse maximum for amorphous aluminoborosilica, indicating that the coating is protective and retained after oxidation. The cross-sectional microstructure of uncoated sample after oxidation is shown in Fig. 7b. As described above, the main part of the oxide scale flakes off the sample during oxidation. A residual oxide scale with a 15 μm thick is observed on the top of the substrate. In addition, due to the spalling of the outer oxides, the sample is fully affected by internal oxidation of the substrate to generate dispersed particles of HfO_2 and TiO_2 due to the penetration of oxygen.

For the coated sample, both the cross-sectional and surface images reveal that the original coating structure is maintained after oxidation exposure as illustrated in Fig. 7c and 7d. In this study, although an aluminoborosilica layer covers most of the conditioned sample, some exposed MoSi_2 is also present (white regions of Fig. 7c). Moreover, the cross-sectional image in Fig. 7d indicates that the microstructure of the

Nb₅Si₃/Nb₅Si₃ composite is unaltered after oxidation exposure. As shown in Fig. 7d, the thickness of MoSi₂ (~25 μm) is maintained which suggests that the recession of MoSi₂ is very small. However, the Nb₅Si₃ layer grows to 50 μm thick after exposure at elevated temperature for prolonged times due to the interdiffusion. Table 2 shows the results of the WDS analysis for the coated sample after oxidation at 1300 °C for 24 h. Upon oxidation, the composition of the outer layer is close to the value for the as-pack sample and it is still composed of MoSi₂ and SiO₂, indicating that this oxidation resistant layer is sustained after oxidation. In the middle layer, 13.72 at.% O is detected, suggesting that this layer is comprised of borosilica as well as (Nb,Ti)₅SiB₂. The formation of borosilica could limit the diffusion of oxygen, resulting in a much slower oxidation rate. The detection of B in the inner layer Nb₅Si₃ suggests that the diffusion of B occurs during oxidation. However, Mo₅Si₃ and Mo₅SiB₂ are not found in the coating. For the Mo-Si-B coating developed on the Mo alloys, the MoSi₂ would convert to Mo₅Si₃ saturated with B and Mo₅SiB₂ upon oxidation [32]. However, this transformation is not observed in this study. The high temperature oxidation performance of molybdenum disilicide has been investigated by Wirkus et. al. [33]. At higher temperatures (1200-1700 °C), the reaction

is favored rather than

It was concluded that the favored reaction at higher temperature might be due to the high permeation rate for Si through MoSi₂ to a Mo-MoSi₂ interface to form the Mo₅Si₃ layer. However, in this study, Si diffuses through MoSi₂ to Nb₅Si₃ during oxidation according to the coating structure of the conditioned sample. As reported by Tortorici and Dayananda [34, 35], the activation energy for the interdiffusion of Si in MoSi₂ and Nb₅Si₃ are 130±20 and 265±30 kJ/mol, respectively. Furthermore, the calculated integrated interdiffusion coefficient of Si in Nb₅Si₃ layer at 1425 °C ($\tilde{D}_{\text{Si}}^{\text{int}}$) is 1.8×10⁻¹² mol m⁻¹ s⁻¹ while that in MoSi₂ at 1350 °C is 1.2×10⁻⁹ mol m⁻¹ s⁻¹. Expressing these values in units of m²s⁻¹ gives interdiffusion coefficients of 1.38×10⁻¹⁶ m²s⁻¹ for Si in Nb₅Si₃ and 2.90×10⁻¹⁴ m²s⁻¹ for Si in MoSi₂. Thus, the

diffusion rate of Si through MoSi_2 to Nb_5Si_3 is much slower than through MoSi_2 to Mo. Therefore, the Mo_5Si_3 is not formed after oxidation due to the low diffusion rate of Si. The reaction (5) is the favored reaction in this study.

Fig. 8 shows microhardness profiles of Nb_{SS} for the $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite, oxidized $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite and oxidized Mo-Si-B coated sample. The microhardness of Nb_{SS} for the oxidized uncoated sample is much higher than that of $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite, while the hardness profile for the oxidized coated sample shows essentially no change compared to the $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite. **Increases in the volume percent of Nb_5Si_3 in Nb-based composites reduce the fracture toughness of the alloy [36]. The fracture toughness of Nb_5Si_3 has been reported to be $\sim 3 \text{ MPa m}^{1/2}$ compared to the fracture toughness of a Nb-18.7Si alloy which is reported to be $12.8 \text{ MPa m}^{1/2}$ [37]. Fracture toughness values for Nb-based in-situ composites have been reported as high as $20 \text{ MPa m}^{1/2}$ [2, 38]. Thus, it appears that the Nb_{SS} is a ductile phase in $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composites and provides room temperature toughness. However, the oxidation resistance of Nb_{SS} in a high temperature environment is poor due to the high solubility of oxygen [2]. When the Nb_{SS} is penetrated by oxygen, the Nb_{SS} becomes brittle and cannot supply room temperature ductility. The similarity in microhardness values of Nb_{SS} for the oxidized coated sample and the $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite indicates that the Mo-Si-B coating protects the $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite from the inward diffusion of oxygen.**

In this study, the $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite is fully protected by the aluminoborosilica glass that forms on the surface of the Mo-Si-B coated $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite sample during oxidation at 1300°C for 24 h. The schematic illustration of the coating structure under different processes is shown in Fig.9. After the pack cementation co-deposition of Si and B, the coating consists of an outer aluminoborosilica layer, a middle Nb_5SiB_2 layer and an inner NbSi_2 layer. After conditioning in air at 1300°C for 2 h, the inner NbSi_2 layer converts to Nb_5Si_3 layer due to the diffusion of Si providing a **good** CTE matching. Upon oxidation at 1300°C for 24 h, the outer oxidation resistant MoSi_2 layer is maintained, and the inner Nb_5Si_3 layer becomes thicker. Since the oxidation protective layer MoSi_2 is maintained in the

coatings after oxidation at 1300 °C for 24 h, this coating is expected to provide protection against oxidation at 1300°C for extended exposure. Cyclic testing of the Mo-Si-B coating on the Nb_{SS}/Nb₅Si₃ composite has not been considered at this time, but is an important testing criteria that should be investigated in the future. However, previous research on Mo(Si,Ge)₂ coatings for Nb show very low mass change (0.59 mg/cm²) for cyclic testing (1370°C, 1 h exposure, 28 cycles) [39]. This shows promise that the Mo-Si-B coating should provide enhanced oxidation protection under cyclic testing conditions.

4. Conclusions

A two-step process has been developed in order to provide a high temperature oxidation resistant coating for a Nb_{SS}/Nb₅Si₃ composite. The Nb_{SS}/Nb₅Si₃ composite samples were initially coated with a layer of Mo through a Mo(CO)₆ decomposition reaction. The second step involved a co-deposition of B and Si by a pack cementation process using a mixture consisting of Si, CrB₂, NaF and Al₂O₃. The resultant Mo-Si-B coating exhibits good adherence to the Nb_{SS}/Nb₅Si₃ composite. Oxidation exposure at temperatures up to 1300 °C demonstrated a mass change of 0.8 mg/cm² for a 24 hour exposure and an unaltered Nb_{SS}/Nb₅Si₃ composite microstructure. Microhardness profiles showed that the Mo-Si-B coating is an effective barrier to the inward penetration of oxygen for Nb_{SS}/Nb₅Si₃ composites. The two-step strategy provided an effective oxidation resistant coating that can enable high temperature use of Nb_{SS}/Nb₅Si₃ composites.

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Figure Captions

Fig.1 Microstructure of Nb_{SS}/Nb₅Si₃ composite with a composition of Nb-15Si-24Ti-4Cr-2Al-2Hf (at.%)

Fig. 2 Surface (a) and cross-sectional (b) BSE images of Mo on Nb_{SS}/Nb₅Si₃ composite substrate using carbonyl process

Fig. 3 (a) XRD pattern from the surfaces of the Mo-Si-B coatings; Surface (b) and cross-sectional (c) BSE images of the coated sample

Fig. 4 Surface (a) and cross-sectional (b) BSE images of the coated sample

Fig. 5. Thermogravimetric analysis of an uncoated Nb_{SS}/Nb₅Si₃ sample and a Mo-Si-B coated sample at 1300 °C for 24 h. O₂ was introduced at a rate of 20 mL/min. The coated sample was conditioned prior to testing.

Fig.6. Photographs of the uncoated (a) and coated (b) Nb_{SS}/Nb₅Si₃ samples after oxidation at 1300 °C for 24 h.

Fig. 7 (a) XRD patterns from the surfaces of the oxidized uncoated and coated samples; (b) cross-sectional BSE images of the oxidized uncoated sample; Surface (c) and cross-sectional (d) BSE images of the oxidized coated sample.

Fig. 8 Microhardness traces as a function of distance from the surface for the Nb_{SS}/Nb₅Si₃ composite, oxidized uncoated and oxidized coated samples.

Fig.9 Schematic illustration of the coating structure (a) as-pack sample; (b) sample conditioned at 1300 °C for 2 h in air; (c) sample oxidized at 1300 °C for 24 h in a thermogravimetric analyzer.

Fig.1 Microstructure of $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite with a composition of Nb-15Si-24Ti-4Cr-2Al-2Hf (at.%)

Fig .2 Surface (a) and cross-sectional (b) BSE images of Mo on $\text{Nb}_{\text{SS}}/\text{Nb}_5\text{Si}_3$ composite substrate using carbonyl process

Fig. 3 (a) XRD pattern from the surfaces of the Mo-Si-B coatings; Surface (b) and cross-sectional (c) BSE images of the coated sample

Fig. 4 Surface (a) and cross-sectional (b) BSE images of the coated sample

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Fig. 8 Microhardness traces as a function of distance from the surface for the Nb_{SS}/Nb₅Si₃ composite, oxidized uncoated and oxidized coated samples.

a		b		c	
Aluminoborosilica		Aluminoborosilica		Aluminoborosilica	
MoSi ₂		MoSi ₂		MoSi ₂	
(Nb,Ti) ₅ SiB ₂		(Nb,Ti) ₅ SiB ₂		(Nb,Ti) ₅ SiB ₂	
(Nb,Ti)Si ₂		(Nb,Ti) ₅ Si ₃		(Nb,Ti) ₅ Si ₃	
Substrate		Substrate		Substrate	

Fig.9 Schematic illustration of the coating structure (a) as-pack sample; (b) sample conditioned at 1300 °C for 2 h in air; (c) sample oxidized at 1300 °C for 24 h in a thermogravimetric analyzer.

Table Captions

Table 1 EPMA analysis for the as-pack sample

Table 2 EPMA analysis for the oxidized coated sample

Table 1 EPMA analysis for the as-pack sample

	B	Si	Mo	Nb	Ti	Na	Al	O	Hf	Cr	Sum
	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(wt.%)
Outer layer	0	62.84	29.28	0.01	0.02	0.89	0.63	6.97	0.00	0.10	98.41
Middle layer	31.88	14.10	0.34	29.90	14.99	0.04	1.22	4.35	0.62	2.54	99.11
Inner layer	0	56.94	0.00	25.12	12.56	0.05	0.63	1.41	0.56	2.36	99.63

Table 2 EPMA analysis for the oxidized coated sample

	B	Si	Mo	Nb	Ti	Na	Al	O	Hf	Cr	sum
	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	(wt.%)
Outer											
layer	0	61.09	28.88	0.90	0.13	0.49	0.15	5.50	0.00	0.23	100.2
Middle											
layer	14.28	35.05	5.64	19.99	10.51	0.05	0.16	13.72	0.27	0.34	101.06
Inner											
layer	5.91	35.22	0	34.95	16.74	0.00	0.07	4.27	1.00	1.87	101.99