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SILICON-TITANIUM CODEPOSITION ON NIOBIUM: PROPERTIES AND BEHAVIOR AT HIGH TEMPERATURES

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Abstract. *Niobium silicide coatings have been studied for their potential application at high temperature components that require resistance to creep and oxidation. However, the difference in the thermal expansion coefficients between $NbSi_2$ and Nb substrate makes niobium silicide coatings susceptible to cracks formation and oxidation at high temperatures. Titanium is frequently added to alloys to increase the toughness of these materials mitigating crack propagation. Therefore, this study investigated how the addition of titanium to the pack mixture impacts properties and high temperature behavior of niobium silicides coatings processed by pack cementantion. Coatings were processed at 1000°C for 6 hours with a pack composition of 15% Si and 10% Ti, using pure niobium as the substrate. After processing, coatings were exposed to a temperature scan up to 1350°C and to isothermal exposures at temperatures of 800°C and 1100°C for 2 hours. Characterization used SEM, EDS, XRD, and microhardness tests to evaluate the properties of coatings. Results showed that Ti did not alter the formation of single phase $NbSi_2$ coatings, with no detectable presence of titanium in the coatings composition. The presence of Ti in the processing does not cause a significant impact on the thickness or hardness of the processed coatings. The weight gain after the scan at 1350°C shows that the silicide coatings processed with titanium have much less weight gain than the silicide coatings with only silicon in the pack mixture. After exposure to isothermal temperature, coatings only exhibited the formation of SiO_2, regardless of the test temperature, confirming the integrity of the coatings.*

Keywords: *silicides, niobium, high temperatures, titanium, pack cementation.*

1. INTRODUCTION

Developing materials for high temperature applications can enhance the efficiency and the performance of many components that operating environment. For instance, gas turbines components particularly those of the hot section should be manufactured with materials that can withstand operating conditions. Consequently, the material must have creep resistance and good oxidation resistance (Boyce, 2002). Although nickel alloys have been used in these applications, there is a limit in the operation temperature due to its melting point. Therefore, refractory metals, such as niobium, have been tested for high temperature applications, above 1300 ºC (Perepezko, 2009). Niobium is a transition metal, extracted from minerals like columbite, tantalite and pyrochlore, whose largest reserves are located in Brazil (Bruziquesi et al., 2019). This metal has many attractive properties that meet the mentioned demands: high melting point (2468°C), low density (8,57 g/cm^3) and good creep resistance at high temperatures (Bewlay et al., 2003). However, niobium alloys show expressive oxidation at low temperatures as from 500°C, a consequence of the formation of Nb_2O_5, which is a problem for the aimed applications (ASM International, 1992) and (Vishwanadh et al., 2013).

In order to enhance oxidation resistance of niobium and niobium alloys there it is the possible to apply coatings or add alloying elements, but the latter has a significant impact in the mechanical properties of the material. Coatings have showed slight effect on the mechanical properties, that is why this procedure is more used to high temperature applications (Zhang et al., 2023). In this context, coatings for niobium have been developed, trying to improve the oxidation resistance at high temperatures. The coating has the purpose of creating a barrier to the diffusion of oxygen, thereby reducing the oxidation of the niobium substrate (Perkins and Meier, 1990). Usually, these protective coatings are intermetallic compounds, such as silicides, which have a good mechanical strength and oxidation resistance. In the case of niobium silicide coatings, the layer of $NbSi_2$ acts as a reservoir of silicon for the formation of a silica (SiO_2) scale. This stable oxide has a protective behavior at high temperatures, with a good adhesion and low growth rate. Because of this, many studies have shown that niobium silicide coatings are a good option to effectively protect against oxidation, providing a smaller interaction between oxygen and niobium.

The Halide Activation Pack Cementation (HAPC) is the most used technique to process silicide diffusion coatings. Essentially, the niobium silicide coating involves the deposition and diffusion of silicon on niobium substrates through chemical reactions in the pack as described in a previous study (Pinto and D'Oliveira, 2021). The substrate, which is the material to be coated, is immersed in a pack mixture composed of powders of an inert filler, an activator halide and the element to be deposited on the surface of the substrate. The coating is processed by a heat treatment in a controlled atmosphere, through gaseous transport and diffusion (ASM International, 1992). For the niobium silicide coatings, processing starts with the decomposition of the chemical activator, for example, the ammonium chloride, which is represented in Eq. (1). Later, with the formation of a gaseous halide, such as the $SiCl_2$, Si is carried to the Nb substrate "Eq. (2)". In the substrate surface this halide is dissociated, "Eq. (3)", enabling a solid-state Si diffusion.

$$NH_4Cl \leftrightarrow NH_3 + HCl \quad (1)$$

$$2\ HCl + Si \leftrightarrow SiCl_2 + H_2 \quad (2)$$

$$SiCl_{2(g)} \leftrightarrow Si_{(s)} + Cl_2 \quad (3)$$

In addition to the $NbSi_2$ layer, niobium silicide coatings can also form Nb_5Si_3 when processed using the Halide Activation Pack Cementation (HAPC) technique. The composition of these coatings depends on the processing parameters, such as temperature and time. The literature suggests that niobium silicide coatings processed above 1200 °C form a dual layer of silicides, $NbSi_2$ and Nb_5Si_3, while coatings processed at lower temperatures only form $NbSi_2$ (Vishwanadh et al., 2013). A niobium silicide coating with a dual silicide structure can be observed in Figure 1.

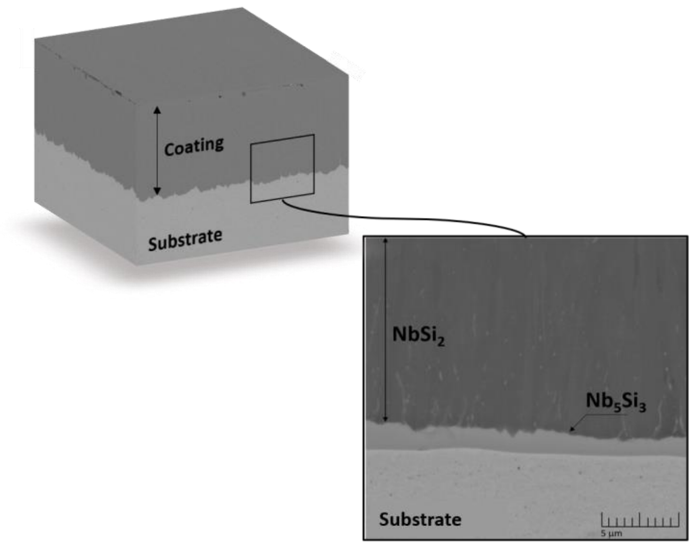

Figure 1. Niobium silicide coating with a dual silicide structure.
Adapted from Pinto and D'Oliveira (2021).

Coatings with a dual layer of silicides exhibit better performance at high temperatures due to their gradient of properties (Xiao, 2006). When the coating consists of only the $NbSi_2$ layer on the niobium substrate, differences in the coefficient of thermal expansion (CTE) between niobium silicides and metallic niobium can result in stress and the initiation of cracks in the coating. The $NbSi_2$ layer has a CTE of 11.7 x 10-6 K-1, whereas pure niobium has a CTE of 7.3 x 10-6 K-1 (Yoon et al., 2005). At high temperatures, this means that the substrate and coating expand at different rates, which can induce cracks on the surface. As a result, with cracks present, oxygen can penetrate the interior of the coating, exposing the substrate and causing rapid oxidation. Therefore, the integrity of the coating can be improved by incorporating an intermediate layer of Nb_5Si_3, which has a CTE of 8.64 x 10-6 K-1, an intermediate value between the previous ones (Xiao, 2006). Another approach to mitigate the formation and propagation of cracks in silicide coatings would be to increase their toughness.

Titanium (Ti) has been added to alloys in order to increase the toughness of these materials, mitigating crack propagation (Zhang; Guo, 2013). When added to the pack cementation process, it is possible to design the codeposition of titanium with silicon in order to enhance the silicide coatings (Glushko et al., 2000). Therefore, this study investigated how the addition of titanium to the pack mixture impacts properties and high temperature behavior of niobium silicides coatings. The objective is to increase the toughness so that crack propagation can decrease, leading to a better coating performance at high temperatures.

2. MATERIALS AND METHODS

2.1 Processing

The substrate of niobium metal (99.8% pure) was supplied by CBMM (Companhia Brasileira de Metalurgia e Mineração) in a metal sheet of 2 mm of thickness. Specimens of 10 mm x 10 mm were cut in the IsoMet 4000 Linear Precision Saw. After hot embedding with bakelite, the surface of specimens was prepared in order to have a more uniform coating. The process included grinding with abrasive paper from a #200 grit to a #1200 grit finish. The bakelite is then removed and to finish, the specimens were cleaned in alcohol with and ultrasonic cleaner for 5 minutes.

To ensure a halide atmosphere in the processing, the Double Pack Cementation technique by Pinto and D'Oliveira (2021) was employed. The pack mixture for the two crucibles was different. For the inner crucible: 15% Si, 5% NH_4Cl (halide activator), 10% Ti and 70% Al_20_3 (inert material that maintains the temperature of the mixture throughout the procedure). Titanium powder had a granulometry between 75 μm and 150 μm and was supplied by the company Brats, while the silicon had a granulometry between 50 μm and 100 μm and was supplied by the company IBFL (Brazilian Ferro Alloys Industry). In the larger crucible, where the intern crucible was immersing, a mixture without titanium was used in order to have a halide atmosphere only. So, the mixture consisted of 15% Si, 5% NH_4Cl and 80% Al_2O_3. Each powder was weighted in a precision scale, placed in a closed recipient and mixed for 1 h. Dehumidification in a furnace for 1h was made in the powder mixture with Titanium.

The two porcelain crucibles were cleaned with alcohol and also put in the furnace at 80°C to dehumidify. The specimens were immersed in the pack mixture in the smaller crucible. In sequence, it was filled with the rest of the mixture and sealed with fire clay mortar to isolate the system and then placed in a furnace at 80°C for 3 hours to dry.

This set was later placed inside the larger crucible, covered with the pack mixture, sealed and dried following the same procedures as for the smaller crucible. Double pack cementation was performed at a chosen temperature of 1000°C for 6 hours in a furnace under argon gas flow. First, a heating ramp of 15°C/min was used, from ambient temperature until the required processing temperature. After reaching the 1000°C, the crucibles were kept inside the furnace for the required period. Lastly, the furnace was turned off and the crucibles were taken out after cooling completely.

2.2 Characterization of the coatings

X-ray diffractometry (XDR) was used to characterize the phases in coating with CuK – α radiation (λ = 1.54060 Å), 20.0 mA and 40 kV. The range variation used is 2Ө between 15° – 100°, being 2°/min.

For scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), a transversal cut was made in the specimens and then this surface was prepared grinding with abrasive paper. This process was made manually, with abrasive paper from #200 grit until #1200 grit, all covered with a thin layer of solid paraffin, to avoid incrustation of this abrasive paper into the niobium specimen. In sequence, polishing with diamond suspensions with granulometry of 3 μm and 1 μm to finish. The microscope used is the scanning electron microscope model TESCAN VEGA3 LMU from the Electron Microscopy Center (CME) of the Federal University of Paraná (UFPR). At the CME, semi-quantitative analyzes of chemical composition are also carried out through EDS using the AZTEC 3.1 SP1 software, Oxford Instruments with an 80 mm² DSS detector. This detector is coupled to the scanning electron microscope.

Vickers microhardness of the coating was measured using a 0.2 kgf load on the cross-section of the entire coating, with a total of 10 measurements. The microhardness tester HMV-2T/Shimadzu was utilized for this purpose.

2.3 Exposure to high temperatures

The processed coatings were subjected to dynamic thermogravimetry analysis (TGA) with temperature ranging from 100 °C to 1350 °C was used with a heating ramp of 15 °C/min in a synthetic air atmosphere. The full temperature cycle lasted 2 h 47 min, including a heating ramp of 1 h 23 min and subsequent cooling to room temperature.

Isothermal exposure of the coatings was evaluated without a controlled atmosphere, during 2 hours, at 800°C and 1100°C. Then, characterization used SEM and XDR in the oxidized specimens to evaluate the coating stability and identify occasional changes with temperature.

3. RESULTS AND DISCUSSION

3.1 Coating Formation

The coating exhibited the formation of silicide phases in the microstructure, with a measured thickness of 32.99 ± 0.46 μm, very similar to coatings processed with only silicon, as reported in the literature, with a thickness of 32.54 ± 2.38 μm (Pinto and D'Oliveira, 2021). The layer of $NbSi_2$ is prominently visible in most parts of the coating (Figure 2 - a), which is consistent with the XRD analysis of the surface (Figure 3). Additionally, a discontinuous layer of the Nb5Si3 phase was identified between the niobium substrate and $NbSi_2$, in agreement with reports in the literature (Vishwanadh et al., 2013). It is worth noting that the literature suggests the formation of this phase typically occurs at temperatures above 1200 °C.

The presence of titanium was not observed within the coating. The chemical composition maps of the silicide coating revealed the presence of titanium only above the $NbSi_2$ layer (Figure 2 - b). However, no peaks indicating the presence of titanium in the coating composition were detected in the XRD analysis of the surface, demonstrating that titanium was not deposited on the niobium substrate. This behavior can be associated with the different partial pressures of silicon halides and titanium halides during processing. Considering that there was no diffusion of titanium into the niobium, it can be said that silicon halides have a higher tendency to diffuse and deposit on the surface of the niobium more readily.

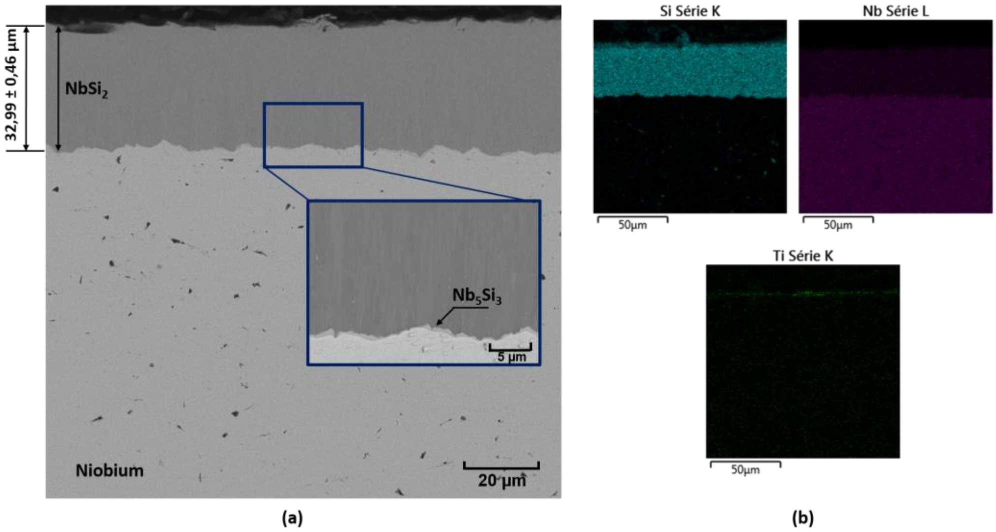

Figure 2. Microstructure of niobium silicides coatings processed with titanium at 1000 °C for 6 hours (a) and chemical composition maps (b).

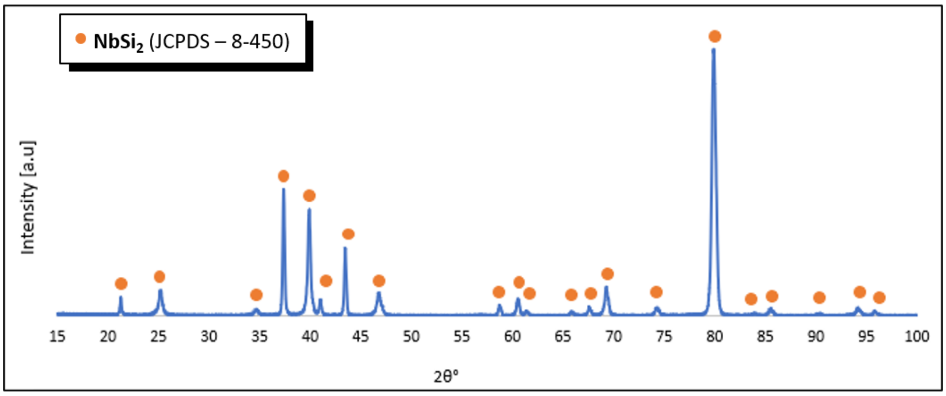

Figure 3. XRD analysis of the niobium silicides coatings processed with titanium at 1000°C for 6 hours.

Although titanium was not identified in the microstructure of the coating, it is possible to observe that the niobium silicide coating processed with titanium in the pack mixture exhibits lower hardness (1101.2 ± 108.52 HV) compared to the coatings processed only with silicon (1221.6 ± 47.8 HV), as reported in the literature (Pinto and D'Oliveira, 2021). This suggests that the presence of titanium in the processing of the coatings may have influenced the formation process of the coating and, consequently, the microstructure of niobium silicide coatings. A more comprehensive analysis of the microstructure of these coatings is needed in order to gain a deeper understanding of how titanium impacts the formation of silicide coatings.

3.2 Behavior at high temperatures

To gain a better understanding of the coating's behavior at different temperatures, a temperature scan up to 1350 °C was carried out on the niobium silicide coatings, as shown in Figure 4. The coatings exhibited a slight increase in weight due to oxide formation. However, in contrast with literature reports for niobium silicides coatings without titanium, this weight gain shows a linear trend within the temperature range of the test (Pinto and D'Oliveira, 2021). This behavior reinforces the hypothesis that the presence of titanium in the processing of niobium silicide coatings alters the microstructure of these coatings, positively affecting the performance of these coatings at high temperatures, which indicates greater efficiency in protecting components for applications requiring high temperature resistance for short durations.

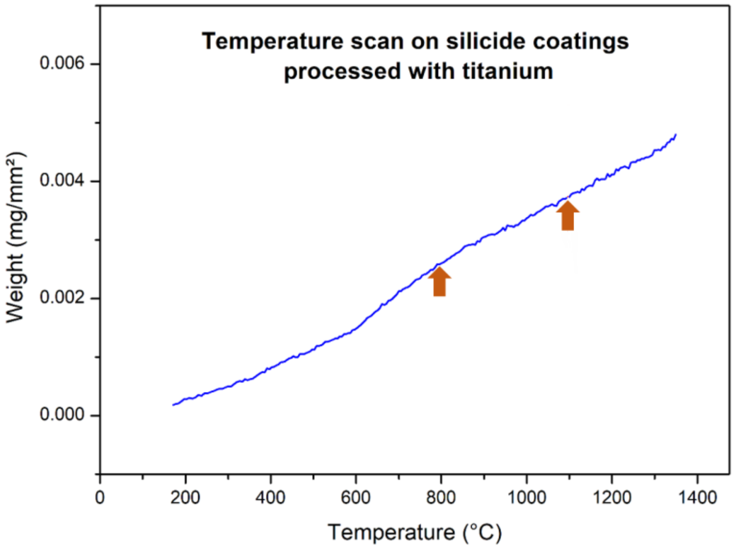

Figure 4. Weight gain of niobium silicides coatings processed with titanium on temperature scan up to 1350 °C.

To analyze the formation of the oxide film on the coating, exposure to temperatures of 800 °C and 1100 °C were carried out. After a two hours exposure period, SiO_2 formation was observed on the surface of the coatings at both temperatures (Figure 5). As anticipated, the coatings exhibited a greater thickness compared to coatings before temperature exposure. The coating exposed to 800 °C had a thickness of 38.49 ± 0.78 µm (Figure 6 - a), while the coating exposed to 1100 °C had a thickness of 41.31 ± 0.5 µm. Furthermore, in both conditions, there was the growth of Nb_5Si_3, which was more pronounced in the coating exposed to 1100 °C (Figure 6 - b). Since there is no additional silicon provided by the pack mixture during the temperature exposure process, the coating undergoes internal diffusion, resulting in the continuous and thicker layer of Nb_5Si_3.

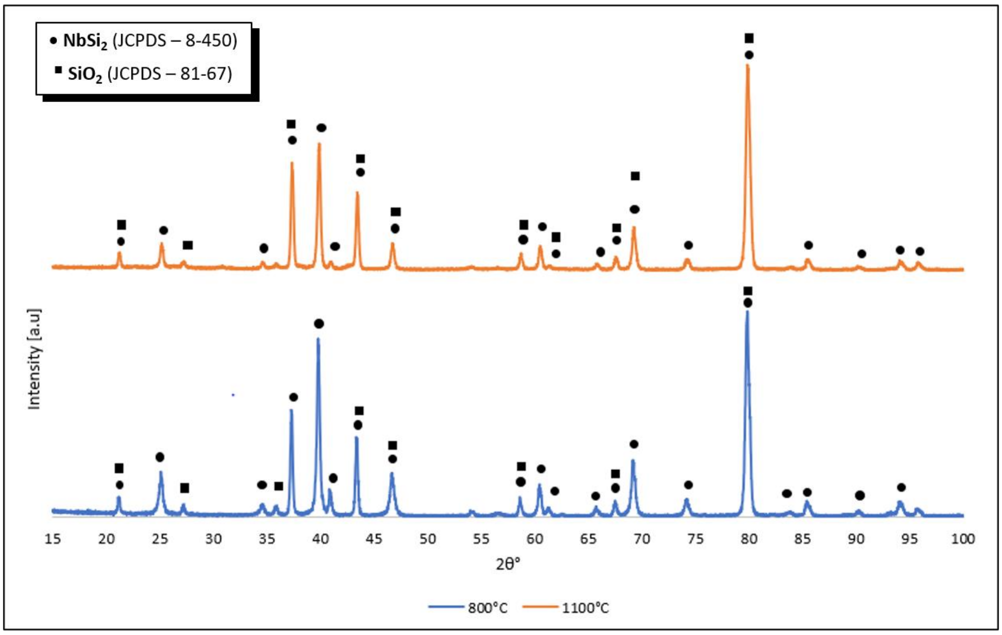

Figure 5. XRD analysis of the niobium silicides coatings processed with titanium after temperature exposure at 800 °C and 1100 °C for 2 hours.

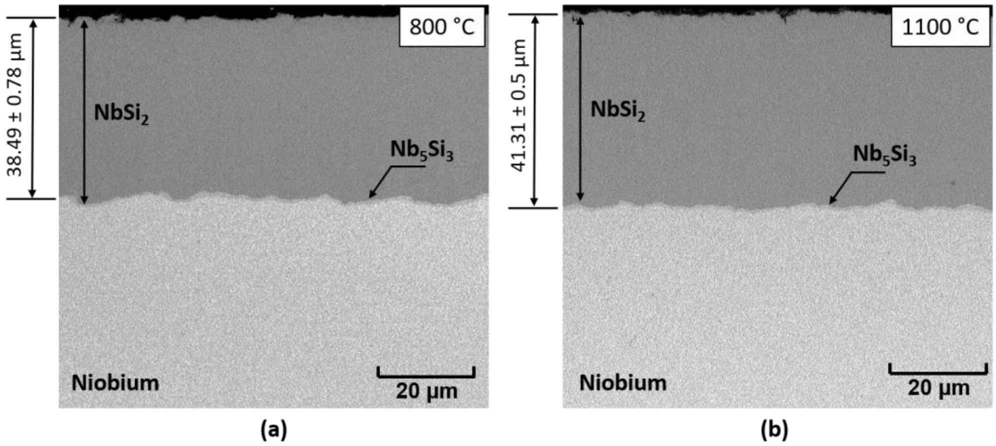

Figure 6. Niobium silicides coatings processed with titanium after 2 hours temperature exposure at 800 °C (a) and at 1100 °C (b).

The integrity of the coatings after isothermal exposure at both temperatures is ensured by the formation of only SiO_2 on the surface of the coatings, with no evidence of the formation of niobium oxide (Nb_2O_5). This information is supported by the consistently low linear mass gain behavior of the silicide coatings processed with titanium when exposed to a temperature sweep up to 1350 °C. If Nb_2O_5 were formed, the mass gain behavior would go from linear to parabolic due to the rapid formation of this oxide (Vishwanadh et al., 2013). The absence of Nb_2O_5 formation also suggests that there were no cracks formed that would have allowed oxygen infiltration down to the substrate. Therefore, titanium, even though not present in the coating composition, likely induced the formation of a niobium silicide coating with greater toughness, as indicated by its behavior at high temperatures.

4. CONCLUSIONS

Coatings of niobium silicides processed with titanium and silicon influences the initial growth of Nb_5Si_3 in these coatings. Despite the presence of titanium in the process, it was not identified in the coatings composition.

These coatings exhibited a linear mass gain behavior when subjected to a temperature scan until 1350°C, which indicates their potential use for applications that expose components to peak temperatures. The weight gain is small with increasing temperature, suggesting their suitability for applications requiring high temperatures for short durations. During exposure to isothermal temperatures at 800°C and 1100°C for 2 hours, the coatings demonstrated the formation of SiO_2, indicating their ability to protect the niobium substrate at these temperatures.

5. ACKNOWLEDGEMENTS

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