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PROCESSING NIOBIUM SILICIDES COATINGS MODIFIED WITH COPPER

Beatriz Aparecida Pinto[1]
Ana Sofia C. M. d'Oliveira[2]
Universidade Federal do Paraná [1,2]
beatriz.aparecida@ufpr.br, sofmat@ufpr.br

Abstract. *Advancements in aeronautical and aerospace industry impose the need for materials that operate effectively in aggressive environments under high temperatures. Niobium is an attractive option for these applications due to an interesting set of properties, such as density similar to nickel superalloys, creep resistance and high melting point. However, the low resistance to oxidation of niobium makes it necessary to apply a protective coating. Silicide coatings exhibit promising results regarding the protection of niobium against oxidation at high temperatures. The attractive behavior is associated with the coating layered structure, of* $NbSi_2$ *and* Nb_5Si_3 *, that act to maintain structural integrity of coatings and to provide Si to form a protective oxide layer (*SiO_2*) under high temperatures. The formation of double silicide layers diffusion coatings high processing temperatures, above 1200 °C, increase the cost of processing making the system more complex to control. An alternative approach to the processing of silicide coatings at lower temperatures would involve the addition of alloying elements in the system that would assist the synthesis of silicides. Extrapolating reports on the effect of Cu, this work analyzes silicide coatings modified with Cu, processed under two different procedures. One of the processing routes, involves the electrodeposition of a copper layer on the niobium substrate before the pack cementation of Si, at 1000 °C for 6 hours. The other approach tested added copper to the Si pack mixture powder and for pack cementation used similar processing parameters. The silicide coatings modified with copper processed with both routes are analyzed through confocal microscopy and microhardness tests, and compared to coatings without copper. Coatings processed with the electrodeposited Cu exhibited a thickness almost tripled of that measured on the non-copper coatings, containing layers with* $NbSi_2$*,* Nb_5Si_3 *and* $Nb_5Cu_4Si_4$*. In contrast, coatings processed by the codeposition of Si and Cu were thinner than the non-copper, exhibiting a* $NbSi_2$ *layer and a* Nb_5Si_3 *layer at the interface with the Nb substrate. The microhardness of the coatings shows that the Cu induced a reduction on the hardness of the* $NbSi_2$ *layer that increases with increasing Cu availability in the system.*

Keywords: *silicides, niobium, copper, high temperatures, diffusion coatings.*

1. INTRODUCTION

The development of materials for industrial applications includes analysis of structure, performance and economic feasibility of manufacturing processes. This scenario motivates a continuous search for enhanced production techniques, in particular those that allow the use of materials under a wider range of high operating temperatures. The challenge of processing of materials for high temperatures applications is strongly associated with the synergy of metallurgical events occurring simultaneously, requiring that materials exhibit a set of complementary properties, such as creep resistance and resistance to oxidation, to operate efficiently in aggressive environments. Frequently, this demanding performance is achieved with the application of protective coatings.

The processing of niobium silicide coatings has been studied extensively for enhanced oxidation protection for niobium alloys, that are susceptible to oxidation at relatively low temperatures (Vishwanadh et al., 2013). At high temperatures, niobium silicides coatings form a protective oxide film (SiO_2) on the surface that prevents the infiltration of oxygen into the niobium substrate (Alam et al., 2010). These coatings can be processed by HAPC (halide active pack cementation) technique, that occurs at high temperature in a furnace. The part to be coated is inserted into a container with the pack mixture, containing the element to be deposited, an activating halide salt and an inert material (Majumdar et al., 2010; Perkins and Meier, 1990). During processing the metal halide vapor reduction reactions deposit Si on the surface of the component followed by solid state diffusion as Si interacts with the metallic substrate. The coating is constitute by one or more layers of intermetallic (silicides) that prevent the diffusion of Si across the full cross section and act as a reservoir that ensure a continuous protective oxide film . (Bianco et al., 1991).

The microstructure of silicide coatings depends on processing parameters such as temperature, time and Si concentration in the pack mixture. For a given pack mixture composition, coatings processed at 1000 °C form a single layer of $NbSi_2$, which acts as a source of silicon for the maintenance of SiO_2 film in high temperature oxidizing environments (Li et al., 2005; Prasad and Paul, 2011; Sun et al., 2019). At processing temperatures above 1200 °C, coatings are composed by two layers, the top layer of $NbSi_2$ and a layer of Nb_5Si_3 at the interface with the niobium based substrate. This coating structure is desirable because Nb_5Si_3 creates a gradient of properties reducing internal stresses that reduce the nucleation of eventual cracks, increasing the service life of the coated component (Pinto and d'Oliveira, 2021; Vishwanadh et al., 2013). The presence of cracks in the coating creates a path for oxygen to diffuse into substrate, causing the component to fail during its operation.

The favorable double-layer silicide coatings require processing at temperatures above 1200 °C directly influencing the competitiveness of the process, as the whole component is exposed to the temperature during processing, processing variables are more difficult to control as diffusion is faster with increasing temperature and higher energy consumption is involved to maintain the high processing temperature. This study is part of an ongoing research that aims at enhancing competitiveness of Si diffusion coatings, in particularly the investigation focuses on the reduction of the processing temperature. The impact of Cu on the rate of silicide formation is discussed against the research of Li et al. (2004), and the efficiency of Cu to allow lower processing temperatures is analyzed.

2. MATERIALS AND METHODS

2.1 Processing

Three processing conditions are used on commercially pure metallic niobium plates, 10 x 10 x 3 mm: niobium silicide coatings (Condition 1) and niobium silicide coatings with copper additions (Condition 2 and 3).

Condition 1: Niobium silicides coatings used a pack mixture with the composition 15% Si, 5% NH_4F and 80% of Al_2O_3.

Condition 2: The co-deposition of copper and silicon was carried out with a pack mixture containing 15% Si, 7% Cu, 5% NH_4F and 73% Al_2O_3.

Condition 3: Pre-deposited layer of copper by electrodeposition on the niobium substrate, followed by pack cementation as in condition 1. The copper electrodeposition solution had the following composition: 150 g/L of copper sulfate ($CuSO_4$), 30 mL/L of sulfuric acid (H_2SO_4) and distilled water.

The substrate to be coated with copper (the cathode) was positioned in the electrochemical cell on the opposite side of the platinum electrode (the anode), at a distance of 20 mm. The 100 mL solution under agitation using a magnetic stirrer during electrodeposition carried out with a constant current density of 5 mA/cm² for a time of 5 minutes, to obtain coating films of approximately 14 µm.

Pack cementation processing was carried out with the following procedures:

Metallic niobium substrates with a surface finish obtained using sandpaper up to #1200 were inserted in a crucible that contained the pack mixture. This crucible was sealed with fire clay mortar and then placed in a furnace for 3 hours at 50 °C to dry the mortar. After drying, this crucible was moved to a larger crucible that also contained the mixture pack, and was also sealed and the set moved to an argon furnace. This double pack cementation procedures are intended to create a barrier to avoid the interaction of the substrate with residual oxygen in the furnace, in the event of the a break in the seal of the smaller crucible (Pinto and d'Oliveira, 2021).

Processing was carried at temperature of 1000 °C for 6 hours, with both heating and cooling rates of 15 °C/min. A furnace with circulating argon atmosphere was used. The set was removed from the furnace and opened at room temperature.

Analyzes of as-processed coatings were carried out by confocal microscopy on the cross section coatings before and after etching in a solution of 20 mL of deionized water, 20 mL of H_2SO_4 and 10 mL of HF. For thickness, 10 measurements were taken in the cross section of the coatings, considering the surface of the $NbSi_2$ layer to the $NbSi_2$/substrate interface or to the $NbSi_2$/ternary layer interface (if any), and from the $NbSi_2$/ternary layer interface to the layer interface ternary/substrate.

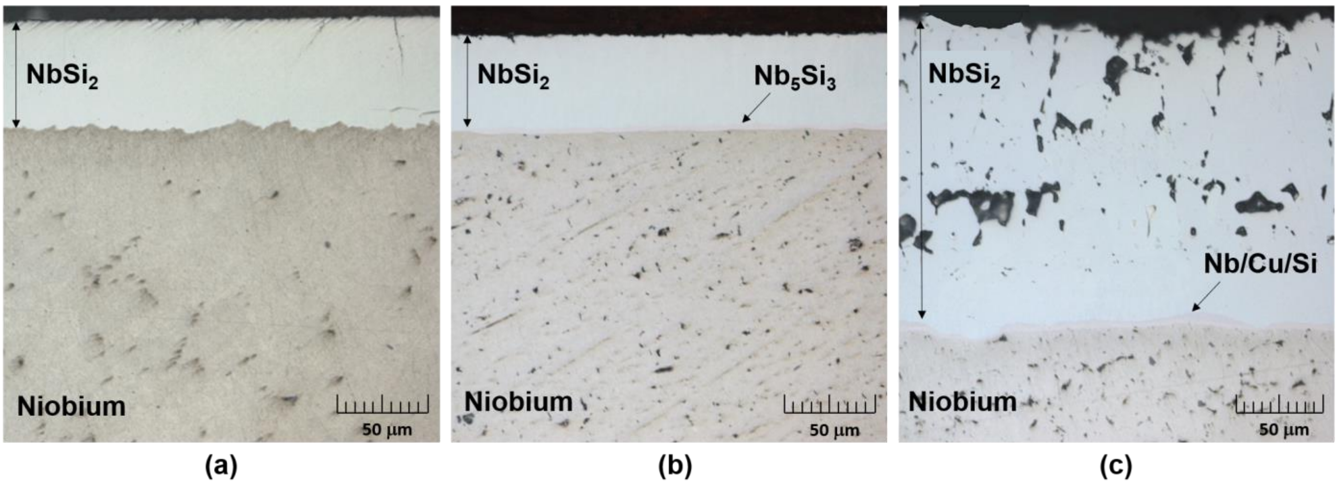
Vickers microhardness measurements of the $NbSi_2$ layer on the cross section of the coatings used a load of 0,025 kgf, on. Ten linear measurements were carried out in the $NbSi_2$ layer, avoiding indentation in areas with pores.

3. RESULTS AND DISCUSSION

Silicides coatings processed at 1000 °C on Nb substrate (Condition 1) exhibited a layer $NbSi_2$, following predictions based on in the literature and on the Nb-Si system diagram for these processing parameters Figure 1-a (Li et al., 2005; Schlesinger et al., 1993; Sun et al., 2019; Vishwanadh et al., 2013).

Silicon and copper co-deposition, Condition 2, resulted on the formation of a $NbSi_2$ layer at the surface and between this layer and the niobium substrate a layer of Nb_5Si_3 formed. Under this processing conditions no Cu rich layer was observed in contrast with results reported by Li et al. (2004) of a Cu rich layer at the $NbSi_2$/Nb interface, The processing conditions used by theses reseachers were similar to those used in our with siliconizing at 1050 °C for 2 hours, using a percentage of 3% copper in the pack mixture and reported a composition of 58% Nb, 41% Si and 1% Cu. Further characterization of the microstructure used a chemical etching, Figure 2, to identify the interfaces between layers in coatings. Analysis showed the Nb_5Si_3 uniform layer at the interface with the niobium substrate and confirmed the lack of evidences of a Cu rich layer.

Procedures adopted in Condition 3 used an electrodeposited copper layer before siliconizing, resulting in coatings that exhibited the $NbSi_2$ layer near the external surface, and a non-uniform Cu rich layer (orange color) at the $NbSi_2$/Nb interface, Figure 3. The latter was described by Pinto (2019) as a ternary compound, with a composition compatible with, $Nb_5Cu_4Si_4$, corroborated by observations on Cu and Si co-deposited coatings reported by Ganglberger (1968). Detailed analysis of these coatings revealed that between the NbCuSi ternary layer and the niobium substrate there is an intermediate layer of Nb_5Si_3. The formation of the Nb_5Si_3 layer in silicide coatings processed at 1000 °C as opposed to the higher temperature of 1200ºC, evidences that copper content at the surface on the electrodeposited layer induced a faster synthesis of this silicide.



Figur*e* 1. Niobium silicides coatings processed without copper (a), with Si and Cu codeposited (b) and with electrodeposition of a Cu layer prior to processing (c).

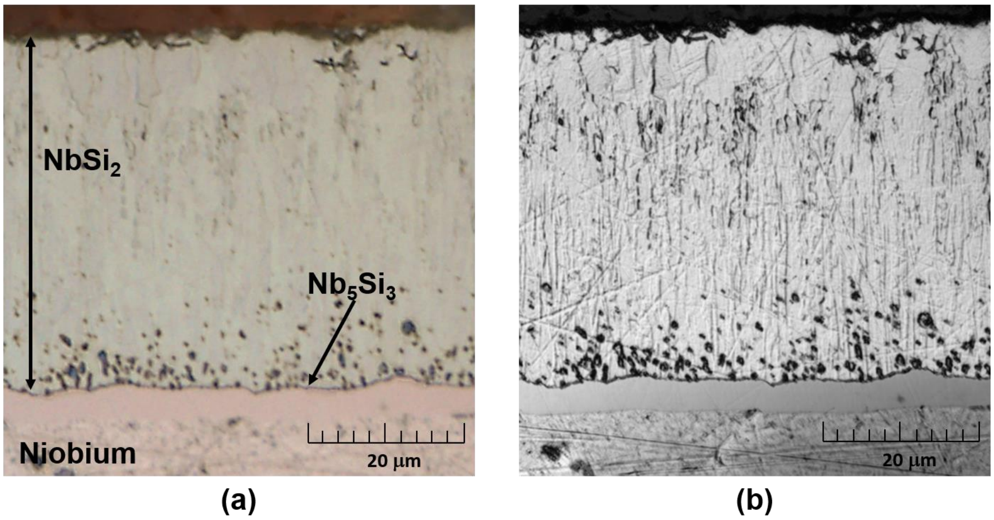
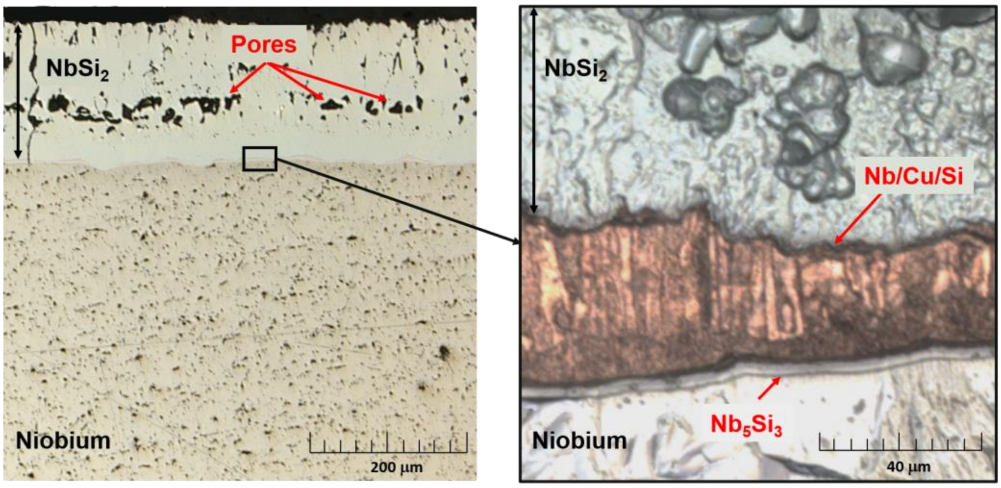


Figure 2. Niobium silicides coatings processed by the codeposition of Si and Cu after chemical etching.



(a) (b)

Figure 3. Niobium silicides coatings processed on an electrodeposited Cu layer, general view of the cross section (a), details of coatings near the Nb substrate (b).

The thicknesses of coatings obtained under the three processing conditions are shown in Table 1. Measurements show that processing conditions impact the thickness of coatings, associated with kinetics imposed by the availability of Si and Cu in each condition. Co deposition of Si and Cu (Condition 2) involves the deposition of Cu and Si at the surface of Nb that depend on the partial equilibrium pressures of the gaseous species (Kung and Rapp, 1989; Majumdar et al., 2006). In addition, it should also be considered the substitutional diffusion into the Nb substrate, together these phenomena account for the measured thinner NbSi$_2$ layer. Inspite of the Nb$_5$Si$_3$ layer formed at the interface with the Nb substrate, coatings processed by co-deposition exhibited a reduction of the total thickness. The presence of Nb$_5$Si$_3$ in these coatings suggests that Cu availability is sufficient to impact the kinetics of the formation of this silicide.

The higher Cu content available in the electrodeposited layer, Condition 3, caused an accelerated growth of the coatings resulting on a total thickness almost three times that of the NbSi$_2$ coatings processed under Condition 1. The formation mechanisms of coatings are not yet well understood, but results suggest that diffusion of Cu into the Nb substrate is facilitated in the co-deposition procedures. Regarding the synthesis of silicides, it is observed that a larger availability of Cu accelerated the synthesis of NbSi$_2$ and allowed for the formation of a thin Nb$_5$Si$_3$ layer.

Table 1. Thicknesses of the layers of the coatings under the three processing conditions.

	Thickness (µm)	
	NbSi$_2$	**NbCuSi**
Condition 1	58,34 ± 1,4	-
Condition 2	46,41 ± 0,75	-
Condition 3	167,75 ± 6,64	34,7 ± 8,59

Further information regarding the impact of Cu in the silicide coatings was gained from microhardness measurements in the NbSi$_2$ layer in coatings, Figure 4. Cu caused a decrease in the microhardness of NbSi$_2$ layer, with the larger availability of Cu resulting in the most significant reduction on microhardness. Further analysis is required to better assess the impact of Cu on the structure of the intermetallic compound. Previous work on the effect of point defect in the ordered structure of NbSi$_2$ revealed that increasing vacancy concentration in the crystal structure causes a reduction in hardness. It is also claimed that Si vacancy are favored due to their higher stability leaving an open question as to which sublattice the Cu atoms would be accommodated. It is of relevance to point out that both coatings containing Cu exhibit porosity, larger pores are observed in the NbSi$_2$ layer near the interface with the Cu rich layer. The smaller porosity near the interface with the Cu rich layer obtained in coating processed by co-deposition of Cu and Si can be related to the Kirkendall effect in agreement with Zeng et al. (2020). The Kirkendall effect refers to the formation of vacancies initially near the surface and as the coatings grows aggregate forming pores that account for the porosity observed near the interface with the Cu rich layer.

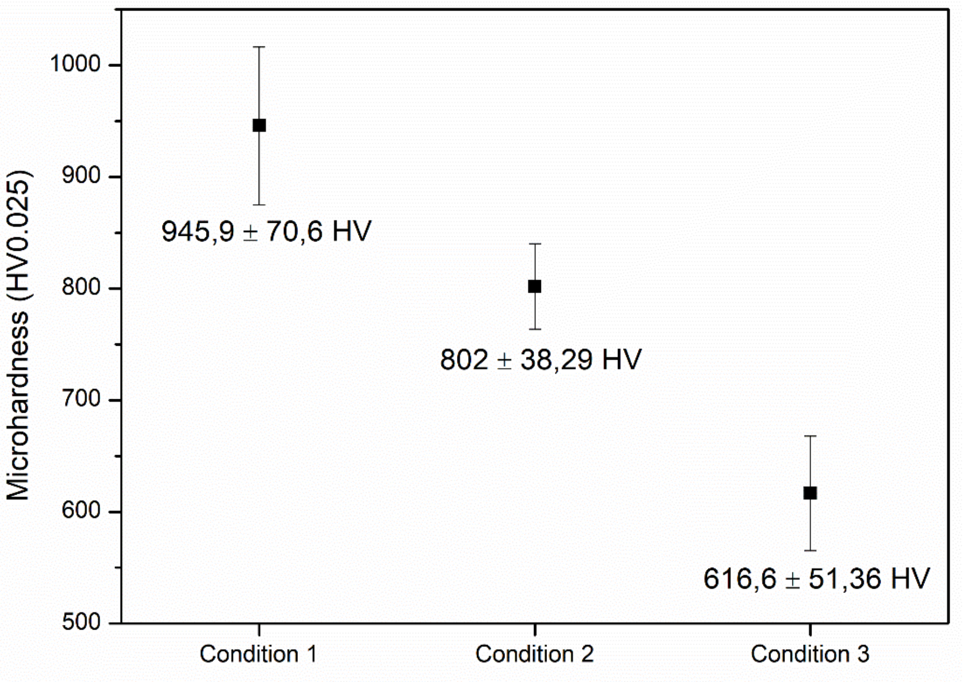


Figure 4. Microhardness of the $NbSi_2$ layer of the coatings under the three processing conditions.

4. CONCLUSION

Under the conditions used in this study of the effect of Cu in the Nb silicide diffusion coatings processed by pack cementation it is possible to conclude that

- Processing route has a strong impact on the availability of Cu in coatings
- Both copper and non-copper coatings result in the formation of a $NbSi_2$ layer at the surface of coatings;
- Coatings processed by electrodeposition of a Cu layer prior to pack cementation, form a ternary layer of niobium, copper and silicon at the interface with the Nb substrate.
- Increasing availability of Cu allows for a thicker $NbSi_2$ layer;
- Coatings processed by the codeposition of Si and Cu form a Nb_5Si_3 layer at the interface with the Nb substrate;
- Larger availability of Cu allows for the formation of a Nb_5Si_3 layer, indicating that the amount of copper in the system influences the synthesis of the niobium silicide;
- Cu induced a reduction on the hardness of the $NbSi_2$ layer that increases with Cu availability in the system, the latter also contributing for the presence of pores near the interface with Cu rich layer.

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