24th ABCM International Congress of Mechanical Engineering
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-1807
PROCESSING AND CHARACTERIZATION OF Si BASED DIFFUSION COATINGS ON METALLIC Nb

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***Abstract**. Refractory metals, such has Nb based alloys have been referred to as the next generation high temperature metals. These alloys have an attractive combination of mechanical properties and a high melting point. However, the application of these alloys is restrained by their reduced oxidation resistance associated with the non-protective nature of Nb2O5. This study addressed this issue, using Si diffusion coatings processed by pack cementation to protect metallic Nb plates. Si diffusion coatings have been reported to have a positive impact on the oxidation resistance at elevated temperatures. The impact of pack composition and temperature on the characteristics of diffusion coatings on metallic Nb plates were evaluated. In the pack procedures with a processing time of 6 hours and pack activator 5 wt.%Nh4Cl were used. Pack composition analyzed processing samples at 1000°C using 10 wt.%Si and 30 wt.%Si. The effect of processing temperature was assessed using this same processing parameters of pack composition at 1150°C. Subsequently, as-processed surfaces were characterized regarding the structure of coatings including chemical composition profile and microstructure of expected intermetallic layers. Results showed that an increase in the silicon content in the pack mixture produced coatings composed of a silicide layer NbSi2. At the higher processing temperature tested, 1150°C, thicker coatings associated with the presence of NbSi2 and a richer silicon phase Nb5Si3 were obtained. However, pack mixture conatining 10 wt.%Si failed to process silicides coatings regardless of the processing temperature used. This worked showed that the processing parameters used strongly influenced the reservoir of Si in coatings, associated with the layered coating structure and silicides phases present, therefore are expected to impact the behavior of Si diffusion coatings.*

***Keywords:** Diffusion Coatings, Metallic Nb, Silicides.*

1. INTRODUCTION

Refractory metals, such as Nb based alloys have been referred to as the next generation high temperature metals. These alloys have an attractive combination of mechanical properties and a high melting point. However, the reduce oxidation resistance associated with the non-protective nature of Nb_2O_5 has restricted high temperature applications (Majumdar et al., 2015).

Silicon diffusion coatings have been reported to have a positive impact on the oxidation resistance at elevated temperatures (Campbel, 2008). Si is deposited at the surface of the alloy and diffuses into the material. The reactivity between Si and Nb results on a continuous layer of silicides, that acts as a reservoir of Si. The SiO_2 oxide layer formed at high temperature prevents the diffusion of oxygen ions through the oxide film to the base material (Vishwanadh et al., 2013). The halide-activated pack cementation is a stablished diffusion controlled process employed to produce a protective coating on high temperature materials (Majumdar et al., 2010). The technique consists of immersing the materials to be coated in a crucible with powder mixture (the pack mixture). In the siliconizing process, the pack contains Si, an activator, which is normally a halide salt (NH_4Cl) and an inert filler material such as alumina, to avoid the coating element source from sintering at high temperature (Mévrel et al., 1986). Many studies have been carried out on diffusion coatings using Al, regarding the effect of processing parameters (time, temperature and availability of Al in the pack mixtures), chemical composition of the alloy being aluminized, oxidation performance, among others. However, Al diffusion coatings are not adequate to protect Nb alloys, that besides having a very high solubility with oxygen, easily form oxides. In contrast SiO_2 films can successfully protect Nb alloys nevertheless only a few studies in the literature discuss the relationship between processing parameters and the characteristics of Si diffusion coatings. This study aims to contribute to this discussion while addressing the effect of processing temperature and the amount of Si in the pack mixture on the characteristics Si diffusion coatings processed on metallic Nb plates.

2. EXPERIMENTAL PROCEDURE

The niobium samples with 10mm x 10mm x 3mm, were cut from the metallic plates supplied by CBMM. To ensure the equality of all samples, the surfaces were ground with 200, 320, 600, 1200 mesh Silicon carbide paper and polished with diamond paste of 1μm. Samples were subsequently washed with alcohol and submitted to ultrasonic cleaning with alcohol for 5 minutes. The same volume of pack mixture was prepared with differences in the Si content were used in the processing, as described in table 1. The same amount of activator was set for the two mixtures, 5 wt%NH_4Cl and the Al_2O_3 content was adjusted to maintain the proportion of the components at 100%.

Table 1. Pack composition used in processing.

	wt.%Si	wt.%NH_4Cl	wt.%Al_2O_3
Pack mixture 1	10	5	85
Pack mixture 2	30	5	65

Alumina porcelain crucibles with lid were previously washed with alcohol, dried in furnace, kept at a temperature of 100 ° C for 1 hour, in order to dehumidify the materials. The crucibles were filled with pack mixture and then Nb plates were placed in the crucible immersed in the pack, according to in-the-pack procedures. After closing the crucible with the lid, the set was sealed using ceramic cement. The sealing was dried in the furnace at 100°C for 2 days. In order to minimize the oxidation of the materials, the experiment was carried out in a furnace with a non-circulating inert atmosphere. After the cement was dried, set was placed in the furnace. Three purges were carried out in a sealed atmosphere with argon 2.2 to reduce the presence of oxygen inside the furnace chamber. Processing parameters were adopted from the work of Majumdar et al. (2015) that produced silicide coatings on the Nb alloy (Nb-1, Cr-0,1, C) with NH_4F as the activator Heating at a rate of 10°C/min from room temperature to the cementation temperature tested: 1000°C and 1150°C, and maintained for 6 hours. After this period, the furnace started to cool down and was turned off at 300°C. At room temperature the seal was broken and the samples removed from the pack mixture. Subsequently, as-processed surfaces were characterized regarding the structure of coatings including chemical composition profile using EDS, microstructure using SEM and X-ray diffraction of expected intermetallic layers.

3. RESULTS AND DISCUSSION

This study was organized in two sections, the first section assessed the effect of the Si content in the pack mixture (10 wt.%Si and 30 wt.%Si) maintaining the processing temperature at 1000°C. The second section evaluated the impact of processing temperature using samples processed at 1150°C and comparing with results from the first set.

3.1 Effect of the Si content

Pack cementation using in-the-pack procedures applied to a niobium plate immersed in a pack mixture containing Si, is expected to form of a compact niobium silicide layer at the material surface (Majumdar et al., 2015), as a consequence of the deposition of Si and subsequent diffusion into the metal to react with Nb and form the mentioned silicide layer.

The pack cementation procedure modified the surface of the Nb plates immersed in the pack 30 and 10 wt.%Si figure 1 a) and b), respectively. Processed layers showed different morphology depending on the Si content in the pack mixture. Coatings processed in packs containing the higher silicon concentration exhibited a uniform and compact layer, in contrast to the thinner and uneven layer obtained after processing with 10 wt.%Si.

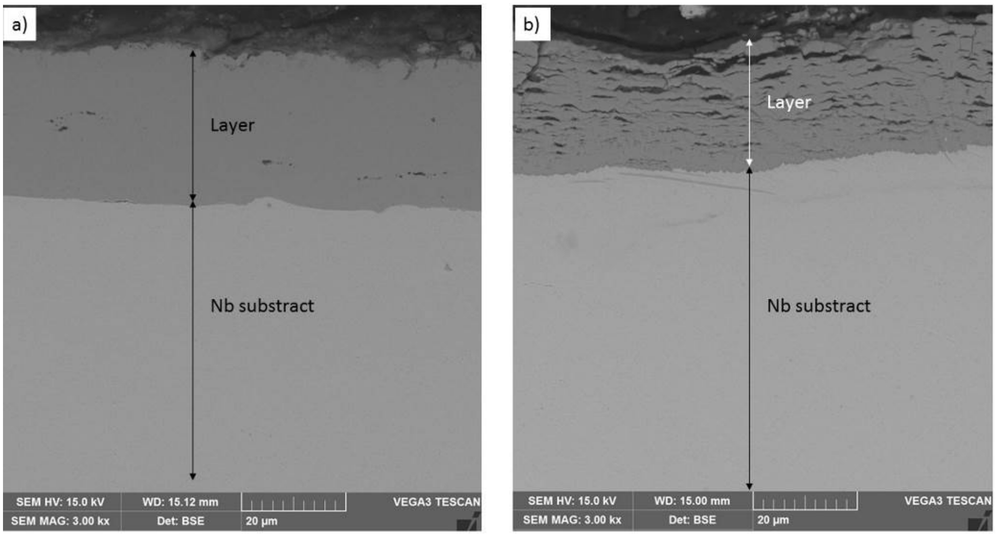

Figure 1. BSE image a) 30 wt.%Si b) 10 wt.%Si in-the-pack, 1000°C, 6h

The EDS mapping, figure 2, confirmed the diffusion of Si into the Nb substract concentrated at the surface. Further analysis using concentration profile confirmed the presence of Si and Nb rich layer on 30 wt.%Si in-the-pack surface, as shown in figure 2. Furthermore, data suggested that, according to the Nb-Si binary phase diagram coatings were composed of the silicide $NbSi_2$.

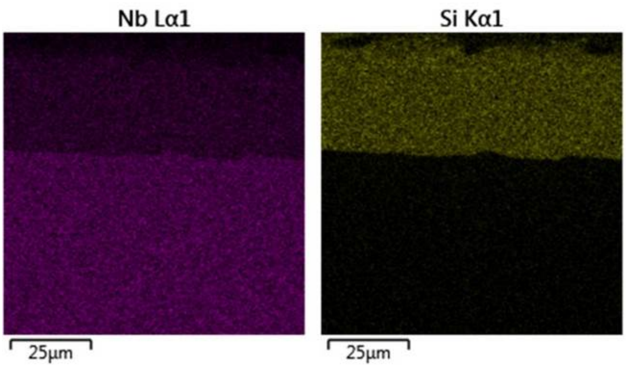

Figure 2. EDS mapping 30 wt.%Si in-the-pack, 1000°C, 6h

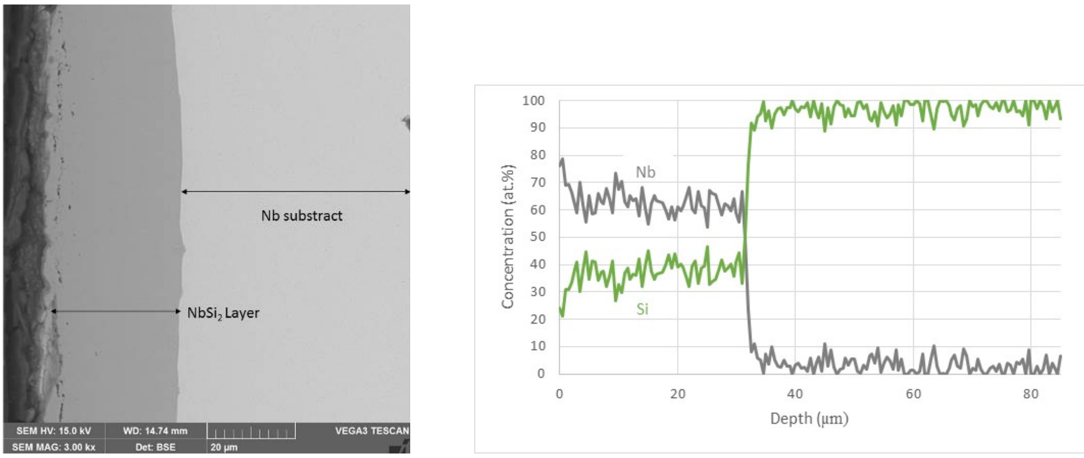

Figure 3. BSE image and concentration profile of 30 wt.%Si in-the-pack, 1000°C, 6h.

In contrast, chemical composition mapping of coatings processed with the pack mixture containing 10 wt.%Si, revealed the uniform distribution of Si at the cross section and the formation of a niobium oxide layer at the surface, figure 4. This result was confirmed by the chemical composition profile, figure 5. Therefore, the continuous Si-rich layer formed at the surface was only identified when processing with the 30 wt.%Si pack mixture. This behavior diverges from data in the literature (Majumdar et al., 2015) although it has to be considered that a different activator (NH_4F) was used in the pack mixture containing 10 wt.%Si, the chemical composition of the substrate was also different (Nb-1, Cr-0,1, C) but the former is considered the key factor for the observed differences.

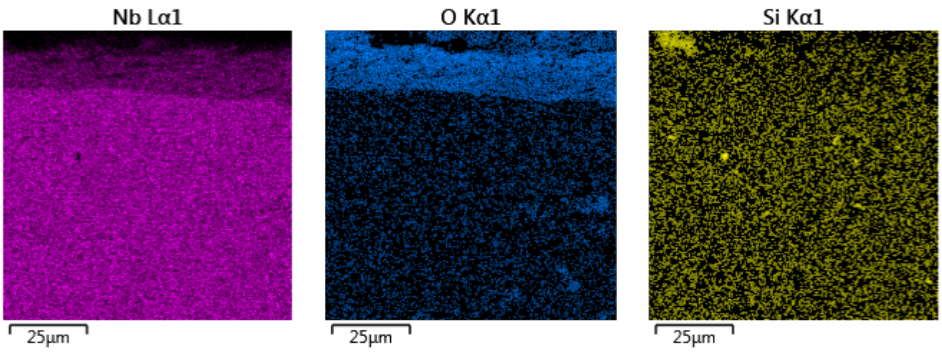

Figure 4. EDS mapping 10 wt.%Si in-the-pack, 1000°C, 6h

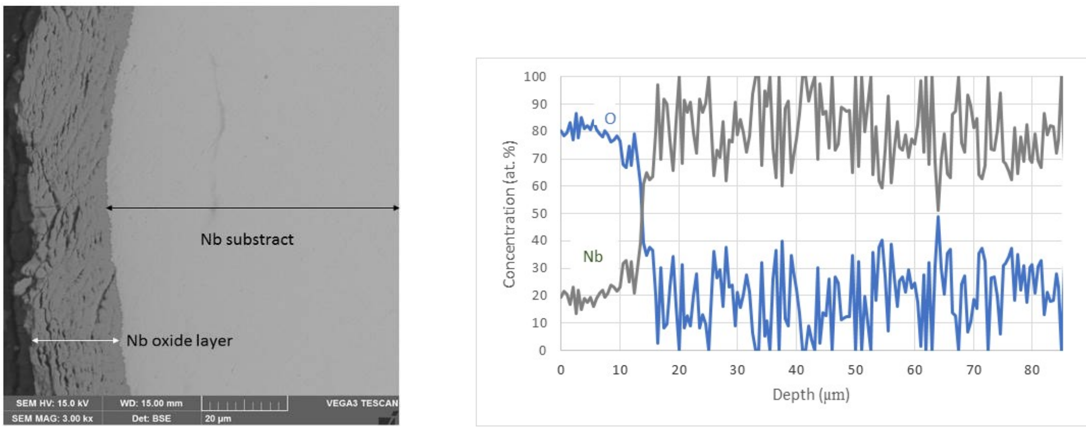

Figure 5. BSE image and concentration profile of 10 wt.%Si in-the-pack, 1000°C, 6h

To assessed the effect of Si in the pack mixture is important to consider the reaction caused by the activator used. In the siliconizing process, initially the metal halides are formed and transported through the gas phase to the substrate surface, as in equation (1) and (2).

$$NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)} \tag{1}$$

$$HCl_{(g)} + Si_{(s)} \leftrightarrow SiCl_{4(g)} + H_{2(g)} \tag{2}$$

The halide dissociates at the surface of the substract and the metal specie is deposited this surface, according to equation (3).

$$SiCl_{4(g)} \leftrightarrow Si_{(s)} + 2Cl_2 \tag{3}$$

Then, the metal diffuses into the substract as. After depositing the metal on the surface, the halogen returns to react with new metal atoms of the powder, maintaining the continuous process.

$$Si_{(s)} + Nb_{(s)} \leftrightarrow NbSi_{2(s)} \tag{3}$$

Pack mixtures containing 30 wt.%Si offer a greater amount of Si atoms to react with the activator, forming the halide vapors that carried and deposited the Si at the surface of the Nb plate. When there is a large compositional gradient between the vapor phase and the material, the diffusion mechanisms are encouraged therefore a large amount of Si is expected to be deposited at the surface. The same principle applies to the solid state diffusion that occurred immediately after the deposition of Si atoms at the surface. Thus, the Si diffusion rate from the surface into the substract is also high, leading to formation of the silicide phase $NbSi_{2,}$ in accordance to the binary phase diagram in figure 6.

Regarding the behavior obtained when processing with the pack mixture containing 10 wt.%Si, the unexpected behavior can be associated with the large affinity of the Nb with oxygen allowing to form oxides as predicted in the Nb-O phase diagram, figure 7. The significant presence of Oxygen in the crucible might be associated with a broken seal or a larger amount of oxygen trapped in the crucible can account for the observed behavior although the latter is less probable, presented on the crucible. Whatever the reason behind the presence of O in the crucible its affinity with Nb player was more significant than the compositional gradient between the Si in the vapor phase and Nb substrate. As a result the substract oxidized preferentially to the diffusion of Si and consequently formation of the silicide.

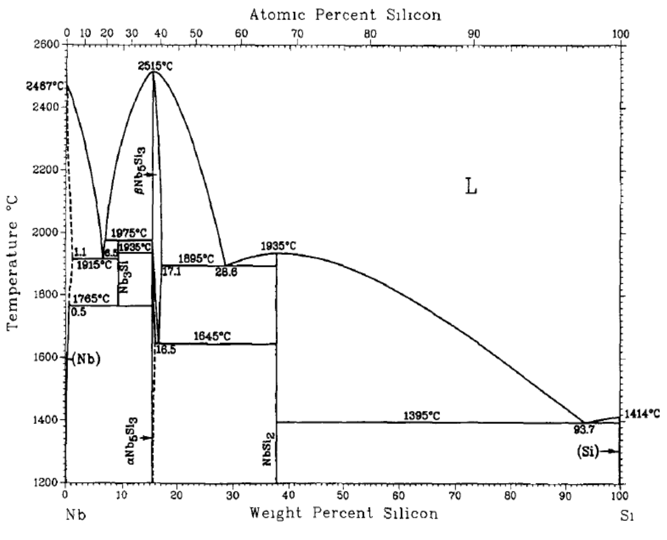

Figure 6. Phase diagram Nb-Si (Schlesinger et al, 1993)

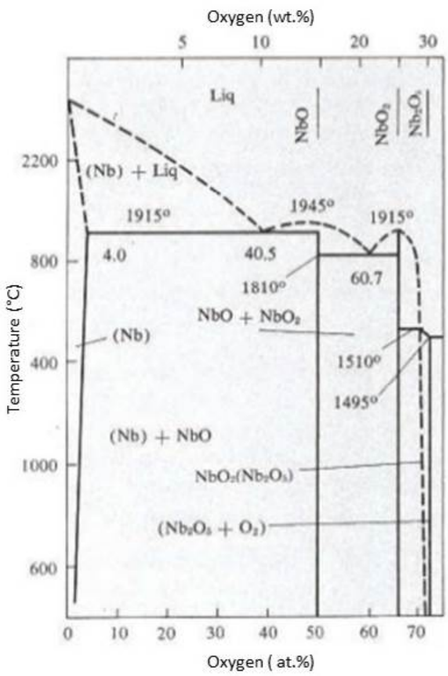

Figure 7. Phase Diagram Nb-O (Lyakishev,1985)

XRD results confirmed previous analysis revealing the presence of the silicide $NbSi_2$ at the surface of samples processed with 30 wt.%Si in the pack mixtures the niobium oxides when processing with the pack mixture containing 10 wt.%Si, figure 8.

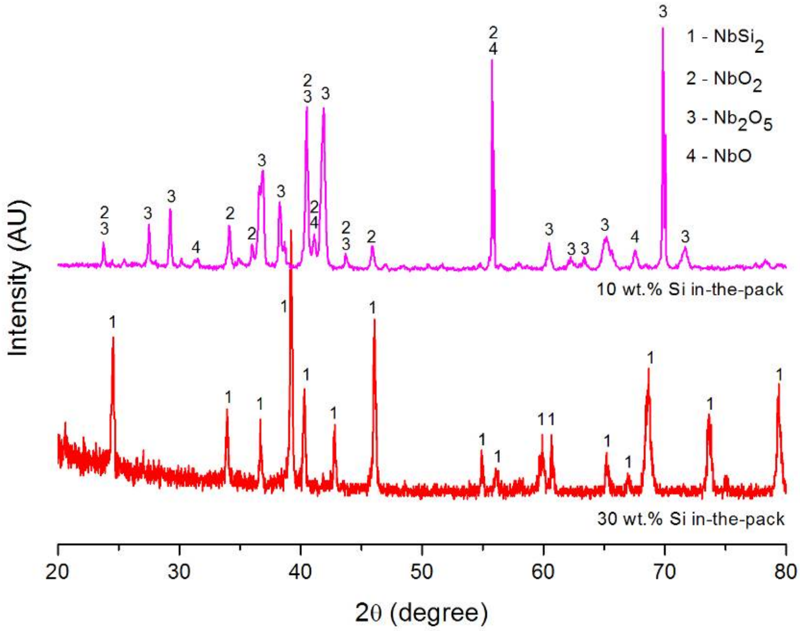

Figure 8. XRD 10 wt.%Si and 30 wt.%Si in-the-pack, 1000°C, 6h

3.2 Effect of the temperature

The impact of temperature on the characteristics of processed surfaces was evaluated using the two pack mixtures, containing 30 and 10 wt.%Si. The processing temperature was increased to 1150°C in order to compare with previous results obtained after processing at 1000°C. An increase in temperature is expected to enhance diffusion mechanisms in the vapor phase and solid-state, as diffusion is a thermally activated phenomenon (Mévrel et al., 1986).

After processing at 1150°C, both pack mixtures resulted on surfaces that exhibited different morphologies and thickness, figures 9 and 10. The 30 wt.%Si pack mixture produced a uniform thicker coating consisting of two layers, that contrasted with the single layer obtained after processing at 1000°C. A two layer coating was also observed after processing with the 10 wt.%Si pack mixture.

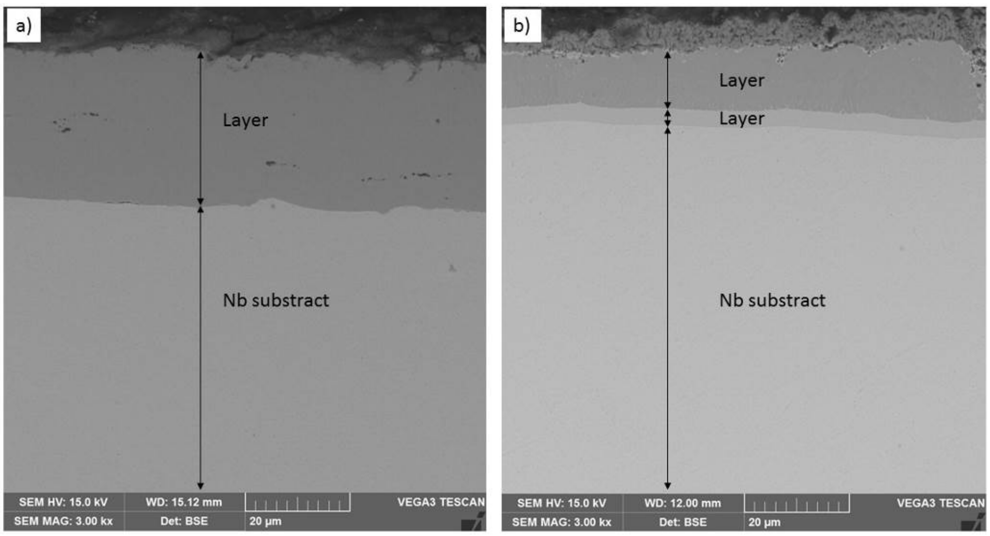

Figure 9. BSE image 30 wt.%Si in-the-pack, 6h a) 1000°C b) 1150°C

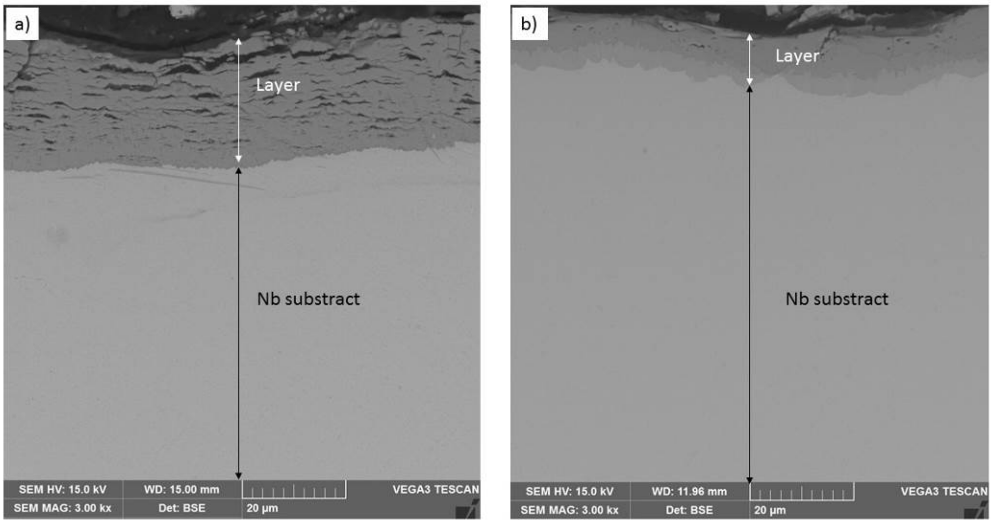

Figure 10. BSE image 10 wt.%Si in-the-pack, 6h a) 1000°C b) 1150°C

The composition profile, figure 11, confirmed the presence of two regions, a Si richer layer (probably associated $NbSi_2$) followed by another Nb richer layer (probably associated with Nb_5Si_3), confirming the presence of both silicides on the surface. EDS mapping confirms the Si-rich layer, figure 12. This behavior contrasted with the presence of single layer of $NbSi_2$ in coatings processed at 1000°C. This behavior can be explained taking into consideration that diffusion is thermally activated, therefore an increase of 150°C in the process temperature of the 30 wt% Si condition enhanced gaseous and solid state diffusion resulting in higher Si deposition at the surface of the Nb surface. The Si concentration gradient is raised between the surface and the substrate, favoring the solid state diffusive flux. To reduce the composition gradient in the substract, solid-state diffusion was more significant allowing to form a Si rich silicide ($NbSi_2$) at the outer layer and a Nb rich silicide (Nb_5Si_3) in the inner layer, both phases predicted by the Nb-Si phase diagram, figure 6. Vishwanadh et al. (2012) observed the silicide Nb_5Si_3 only in temperatures above 1300°C in a Nb alloy (Nb-1, Zr-0,1, C) with pack composition of 85 wt.%Al_2O_3, 10 wt.%Si and 5 wt.%NH_4F, showing the need to have the appropriate temperature and Si concentration for the synthesis of Nb_5Si_3.

Both parameters tested in this study, Si content and temperature, influenced the diffusion of Si towards the surface and into the Nb plate. Contrasting with these results, the higher processing temperature did not change results obtained after processing with pack mixtures containing 10 wt% Si at 1000ºC. The composition profile, figure 13, revealed the presence of oxides at the surface of the Nb plate, which was confirmed by the EDS mapping, figure 14. The oxygen atomic percentage drops across the layer suggesting distinct oxides layers. The affinity between niobium and oxygen was greater than the composition gradient between the surface and substract, leading to the formation of the oxide layer.

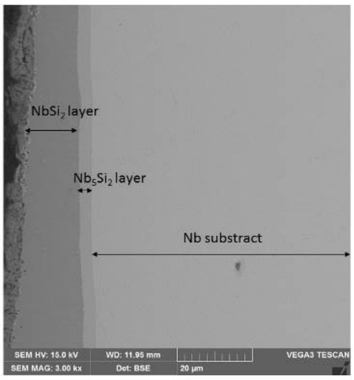

Figure 11. BSE image and concentration profile of 30 wt.% Si in-the-pack, 6h, 1150°C

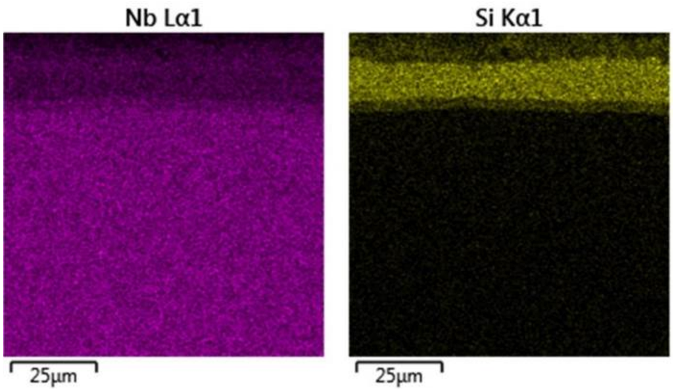

Figure 12. EDS mapping 30 wt.%Si in-the-pack, 6h, 1150°C

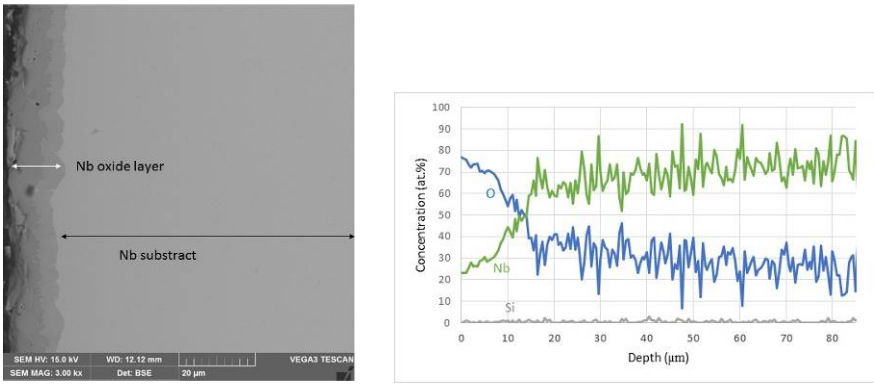

Figure 13. BSE image and concentration profile of 10 wt.%Si in-the-pack, 6h, 1150°C

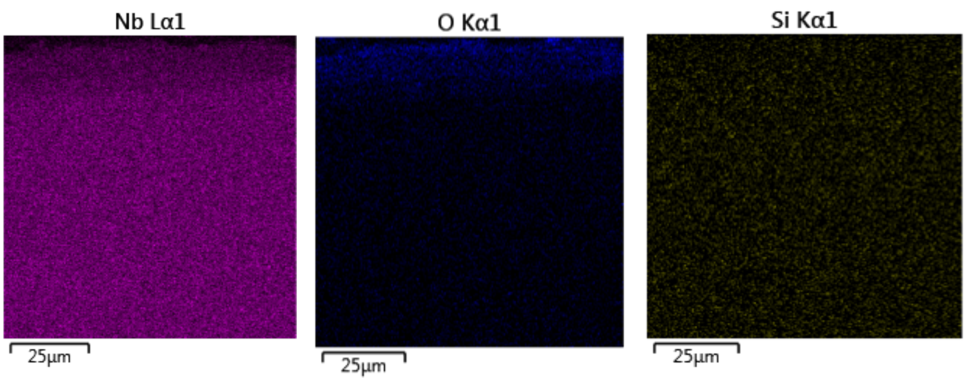

Figure 14. EDS mapping 10 wt.%Si in-the-pack, 6h, 1150°C

Analysis of the XRD results confirmed previous discussion revealing the presence of silicide $NbSi_2$ and Nb_5Si_3 at the surface of coatings processed with 30 wt.%Si in the pack mixture at 1150°C, figure 15. The same can be said for the surfaces processed with 10 wt.%Si in the pack mixture, that showed niobium oxides after processing with both temperatures, figure 16.

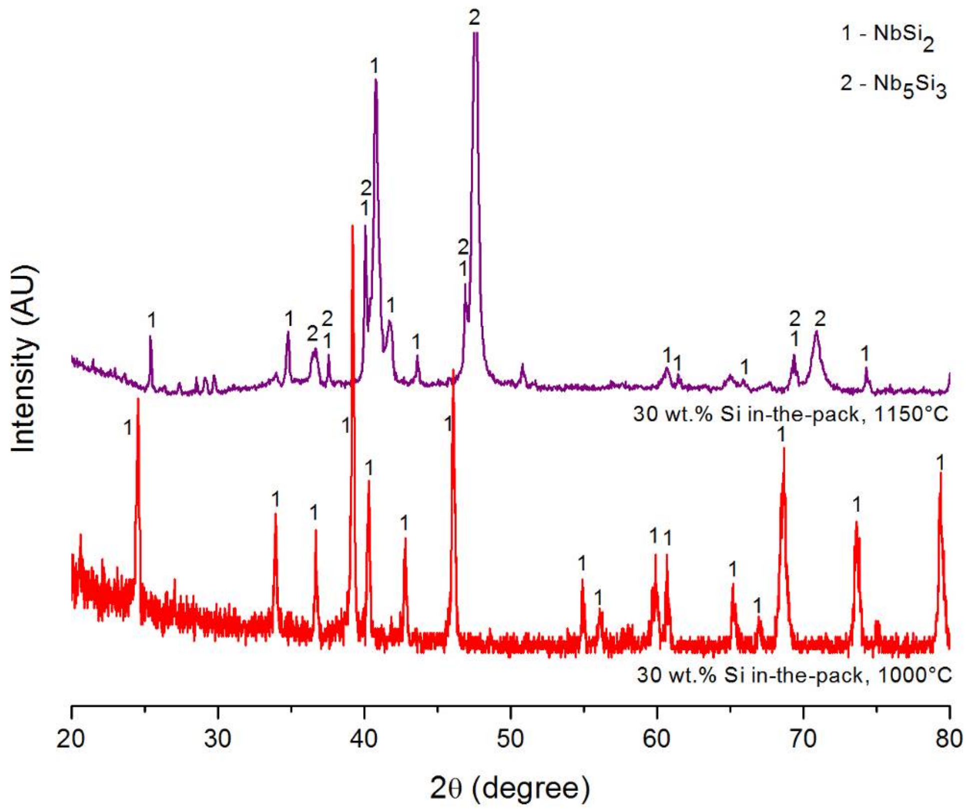

Figure 15. XRD 30 wt.%Si in-the-pack, 6h, 1000°C and 1150°C

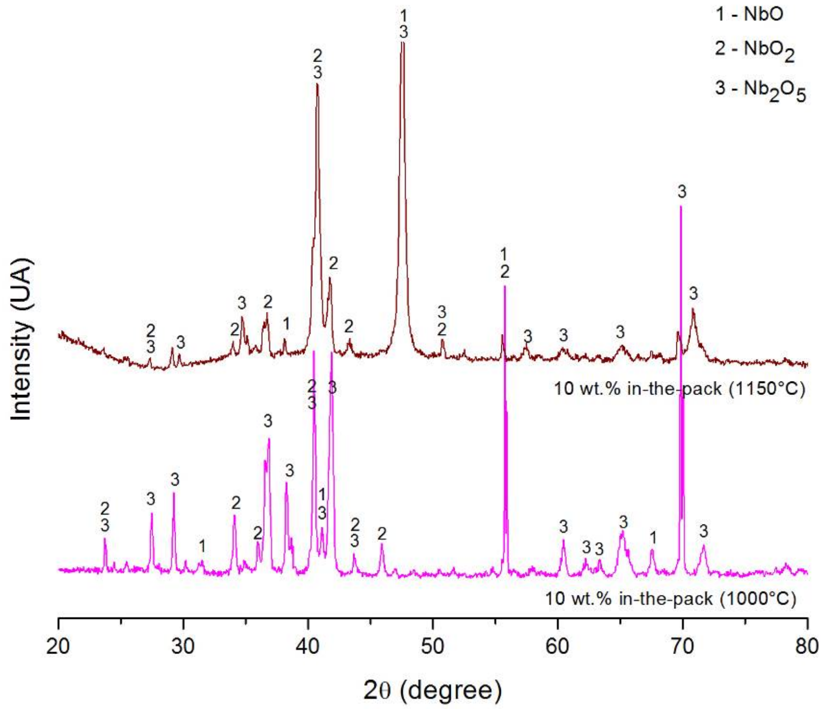

Figure 16. XRD 10 wt.%Si in-the-pack, 6h, 1000°C and 1150°C

4. FINAL REMARKS

For the conditions tested in this study regarding the effect of Si content in the pack mixture and the processing temperature on the characteristics of diffusion coatings on Nb plates, the final remarks are:

- A continuous silicide layer of $NbSi_2$ was obtained after processing with pack mixtures containing 30wt%Si at 1000ºC
- Increasing processing temperature to 1150ºC resulted on diffusion coatings exhibiting a double layer, consisting of a continuous $NbSi_2$ layer at the external surface and a Nb_5Si_3 layer at the interface with the Nb substrate
- Processing with pack mixture containing 10 wt.%Si did not allow for the formation of silicides and regardless of the processing temperature used Nb oxides were identified at the surface of Nb plates

5. ACKNOWLEDGEMENTS

CAPES and CNPq to support this project, CBMM and Rima for providing the Nb and Si metallic.

6. REFERENCES

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7. RESPONSIBILITY NOTICE

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