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FABRICABILITY OF NIOBIUM SILICIDES WITH POWDER PLASMA TRANSFERRED ARC

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Abstract. The low fabricability and poor oxidation resistance challenge research and development on Niobium and Niobium alloys since the golden age of the refractory metals, in the 50's. The difficulties in fabricating these materials by conventional processes challenged their application and reduced competitiveness compared to the other available high temperature materials. However, with the event of Additive Manufacturing (AM), together with new software and computational methods, make the manufacture of Niobium based refractory components increasingly viable. Furthermore, in-situ synthesis of low toughness compounds during the deposition of mixtures of elemental powders might bring an alternative route to process additive manufactured refractory alloys parts. The literature requires more studies exploring the potential of additive techniques as a path to process Niobium and Niobium alloys. This study explores the fabricability of Niobium Silicide alloys by Powder Plasma Transferred Arc (PTA-p) and extrapolates the developed procedures to additive manufacture. The aim is to simultaneously perform the in-situ synthesis of the material and the manufacturing of the component. Results revealed that in-situ alloying was successfully achieved during the multilayer deposition of elementary powder mixtures. The correlation between processing and microstructure of multilayers was assessed and discussed aiming at defining processing conditions for Nb silicide based materials.

Keywords: *Fabricability, Niobium, in-situ synthesis, Additive Manufacturing*

1. INTRODUCTION

For many years refractory alloys were explored with the aim to design high-strength alloys for very high temperatures. Niobium (Nb) is referred to as the most promising refractory material due to its low ductile-to-brittle transition temperature (DBTT) relatively low density (8,48g/cm^3) and high melting point (2745ºC) (Shabalin 2014; Bedford et al. 1996). However, the poor fabricability and low oxidation resistance still impose many challenges (Philips, Carl, and Cunningham 2020).

The availability of Additive Manufacturing (AM) techniques, together with new software and computational methods, make the manufacture of Niobium based refractory components increasingly viable (Ghosh and Olson 2007). Also, in-situ synthesis of low toughness compounds during the deposition of mixtures of elemental powders might bring an alternative route to process additive manufactured refractory alloys parts. However, more studies are required exploring the potential of additive techniques as a path to process Niobium and Niobium alloys.

To achieve high performance at high temperatures, alloying Niobium is mandatory. MATHIEU et al. (2012) reported that silicon is the most suitable alloying element to be added to Niobium exhibiting a two-fold effect, the formation of silica scale at high temperatures and the synthesis of silicide compounds, improving oxidation and creep resistance, respectively. High strength silicides together with a ductile Nb-based solid solution provide a tough material with a good balance between high and low-temperature strength. Nb–Si alloy system can provide good "in-situ" composites, with a variety of microstructures and properties (Kim et al. 2001).

Powder Additive Technologies allows in-situ synthesis of complex alloys during the processing of elemental powder mixtures. This technology also allows to gradually change composition layer by layer to build a functionally graded component. Few studies have been published on AM for pure Niobium and Niobium alloys, but the results confirmed AM as a promising approach for processing these materials (Philips, Carl, and Cunningham 2020; Allen et al. 2019; Guo et al. 2018). Plasma Transferred Arc is the only arc process that uses powdered material and allows the use of elemental powders mixtures to induce in-situ synthesis of hard and low toughness compounds. Menegotto and d'Oliveira (2017) working with Niobium Silicide coatings observed that it is not always that the synthesis of compounds is complete during deposition. Therefore, processing multilayers might bring better results to this procedure.

This work is part of an ongoing project that aims at processing Nb silicides by additive manufacturing. At this stage it is aimed to fill the gap in the literature regarding the fabricability of Nb-Si based alloys, using in-situ synthesis during deposition of powder mixtures by Powder Plasma Transferred Arc. In particular the target is to establish the relationship between the powder mixture chemical composition, processing conditions and microstructure of Nb silicide multilayers

2. METHODS

Elemental metallic powders of niobium, silicon and aluminum, were used to prepare the mixtures Nb37Si and Nb26Si11Al (wt%) with the aid of a precision scale and a Y mixer. The flowability of niobium powder mixtures is an important feature of the process since the PTA equipment depends on the free flow of the feedstock so that it can reach the plasma arc properly. It is worth mentioning that many features can influence the flow of the powder, among them: humidity, morphology, particle distribution, etc.

The morphology of the powders is irregular, which may hinder the flowability during deposition. To assess the flowability of the powder mixtures, the angle of repose was analyzed using the fixed-height cone method, shown in Fig. 1, in which the powder is allowed to flow through a funnel placed at a fixed height until the top of the cone formed by the powder reaches the bottom tip of the funnel (ASM International 1998). The tangent of the angle of repose (alpha) is the ratio of the height of the cone to the radius of the base of the cone. In this work, a height of 2cm was fixed. Angles are recommended to be equal or less than 41º (Mandal, 2015).

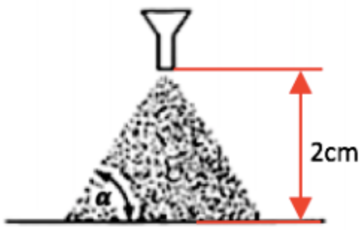

Figure 1 – Fixed high cone method used to assess the flowability of the powder mixtures.

Before deposition, the mixtures were dried in a furnace at 105ºC for 24h in order to remove the excess moisture content of the powders, thus reducing the influence of this oxygen source on the processing. In addition, drying the powders contributes to the most adequate flow of the mixture in the PTA equipment. The substrate was commercially pure metallic niobium to avoid the influence of others elements that could be diluted from the substrate to the builds.

Depositions were made both in a controlled atmosphere and in a protective atmosphere (Argon 2.0) to verify the effects of minimizing the oxygen concentration in the atmosphere on the in-situ alloying and the microstructure soundness. The argon atmosphere was selected due to the great affinity and solubility of oxygen in Nb (Elliott, 1960).

For processing in a protective atmosphere, PTA Starweld 300 equipment was used in the set up shown in Fig. 2. Oxygen levels were monitored inside the protective chamber by assessing the constant gas flow leaving the chamber. At the beginning of the deposition of each layer, the oxygen content was kept under 53ppm.

Differentiated parameter were necessary to process the binary alloy inside the argon chamber due to its worse flowability together with the positive pressure inside the chamber. After the deposition of each layer, an interval of 60s was determined to start the next deposition, in order to avoid the cooling of previous layers, maintaining the influence of each new thermal cycle as similar as possible. The 60s wait was also necessary for the stabilization of oxygen levels in the controlled atmosphere. Single deposits multilayers with a length of 10 cm allowed the characterization of multiple samples.

For microscopy analysis, samples from the cross section of each multi-layer were prepared using silicon carbide sandpaper following the sequence: 220, 320, 400, 600 and 1200 mesh. The grounding was carried out manually by varying the position of the sample by 90° between each sandpaper. Afterwards, 1μm diamond suspension was used to polish samples with a velvet cloth. The chemical etch was done by immersion for 30 seconds in a mixture of 20ml of HF, 15ml of H2SO4, 5ml of HNO3 and 50ml of H2O.

Microstructures were analyzed by Scanning Electron Microscopy with EDS mapping. In order to identify phases, textures and eventual residual stresses, X-Ray Diffraction (Shimadzu XRD7000) scans were performed on top of the multilayers. The semi-quantitative analyzes of chemical composition by EDS and mapping of the chemical composition of the microstructure were performed in a Scanning Electron Microscope of the UFPR Electron Microscopy Center.

Figure 2. Set up of the Starweld machine

3. RESULTS AND DISCUSSION

Analysis started by the flowability of Nb-based powder mixtures. The resting angle of (30°) of the atomized alloy, IN625, was used as a reference, since it allowed the deposition of continuous layers, with excellent finishing and even powder melting (Cardozo et al. 2019). The elementary powder mixtures showed differentiated flowability, with an angle of repose varying between 36°, Fig. 3 (a), and 38°, Fig. 3 (c) which was reflected in the flow through the PTA feeding system and in the inlet of the powder in the plasma arc. The higher angle of repose of the elementary powder mixtures compared to atomized alloy are due to the characteristics of each powder that includes geometry and the ability of the particles to agglomerate. Inconel 625 powder particles are spherical in shape, whereas the elemental powders have an irregular shape. Spherical particles are easier to flow through the system and generally provide a smaller angle of repose compared to irregular particles.

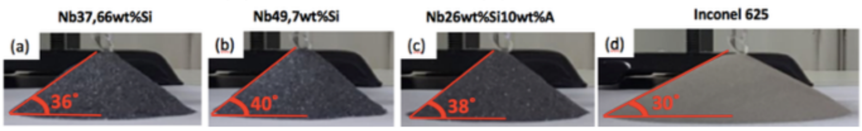

Figure 3. Angle of repose for each powder mixture.

The region where the powder enters into the plasma column can influence the heating rate and temperature of powders, their melting and the soundness of the deposited layer. Figure 4 outlines the influence of the angle of repose in the inlet of the powder into the plasma column for the atomized alloy (30°) and for the mixtures of elementary powders (~40°), keeping the other parameters fixed such as the distance between torch and workpiece and carrier gas flow (Díaz, Dutra, and D'Oliveira 2011). For elementary powder mixtures, the greater angle of rest induces its entry into the plasma column in regions closer to the melting pool or even directly into the melting pool, thus absorbing less arc energy. This factors considerably increase the possibility of the incomplete synthesis and even the lack of fusion of the mixture of elementary powders because there is not an adequate use of the energy from the plasma arc.

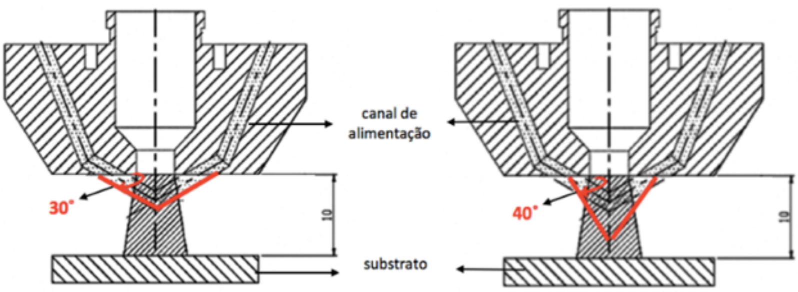

Figure 4. Influence of the feedstock angle of repose on the path from the nozzle to the melting pool.

In order to optimize the mixture flow in the PTA equipment during depositions, high energy densities were required, and high gas feeding flow were required to process into the argon chamber. The multilayers were deposited and their characteristics are dependent on the chemical composition and processing environment. The in-situ alloying succeeds for both powder mixtures, as show the XRD made on the top layer of multilayers processed with the binary, Fig.4, and ternary powder mixtures, Fig. 5.

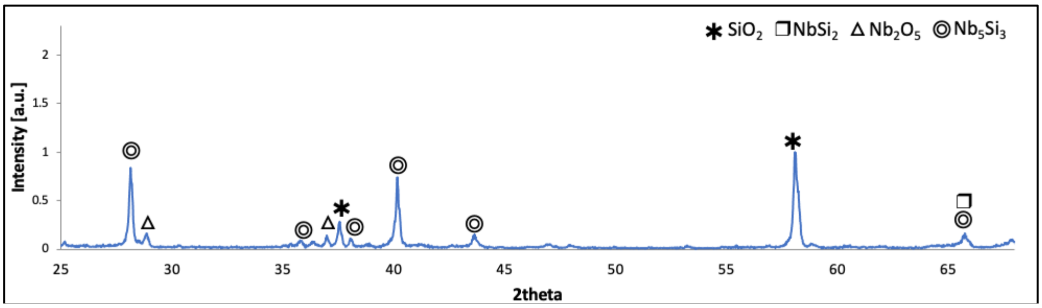

Figure 5. XRD from the top of the multilayer processed with the Nb37%Si mixture in air.

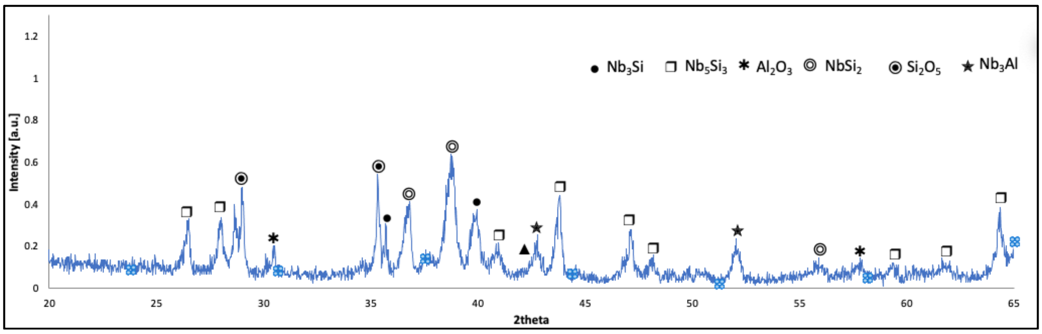

Figure 6. XRD from the top of the multilayer processed with the Nb26%Si11%Al mixture in air.

Nb and Si content measured across layers reveals a much higher Nb content than that in the powder mixtures. This is a consequence of the dilution with the Nb substrate plate that also accounts for the Nb profile that increases towards the first deposited layer at the bottom of the wall, Figure 7. A sharper Nb gradient across layers is produced when processing in argon environment, which can be related to the different processing parameters, particularly the slower scan speed and higher feeding gas flow.

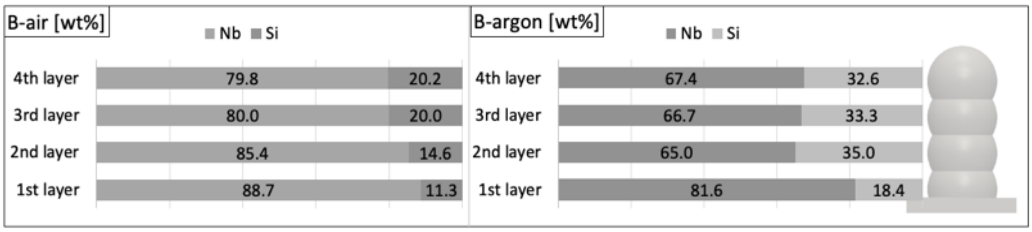

Figure 7 - Composition gradient of the binary multilayers.

Multilayers processed with the ternary powder mixture, Nb-Si-Al, exhibited a very smooth composition gradient across layers, Fig. 8, and a much richer Nb content compared to that of the deposited powder mixture. This is a consequence of the higher heat input imposed by the processing parameters that contributes to high dilution with the Nb plate used as substrate, together with the heat released during in-situ synthesis of silicides (ΔHNb5Si3= -58.5kJ/mol; ΔHNbSi2= -49.9kJ/mol) (Papadimitriou et al. 2014).

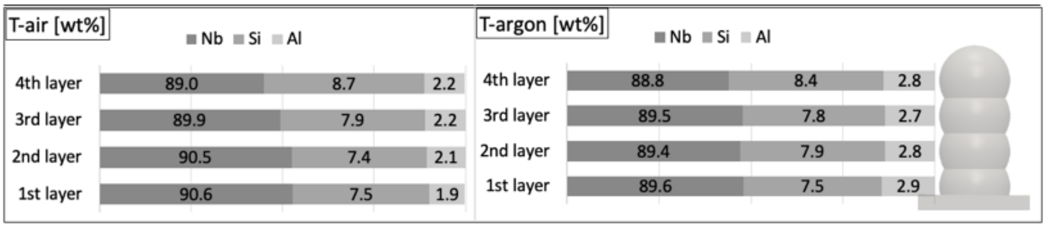

Figure 8 - Composition gradient of the ternary multilayers.

Cross-section analysis of the microstructures at top layer processed in air, Fig. 9, revealed different features particularly regarding the toughness and phase distribution. The binary mixture, Fig. 9 (a), resulted in cracks and the formation of oxide particles within $NbSi_2$ phase. Two distributions of cracks are identified: small cracks that cross Nb_5Si_3 grains, connecting small oxide particles in adjacent $NbSi_2$ grains, and large cracks along $NbSi_2$ grains. The crack distribution is related to the residual stresses generated during the deposition and also to the different Coefficient of Thermal Expansion (CTE) of silicides and oxide fragments (Novak 2010; Schneibel et al. 2002). In contrast, multilayers processed with the ternary powder mixture Nb_5Si_3 dendritic structure with an interdendritic eutectic containing Nb_{ss} containing a dispersion of Al_2O_3. This build showed a small and reduced number of cracks confined in the Nb_5Si_3 dendrites, shown by Fig. 9 (b). The eutectic Nb_{ss} contributing to mitigate crack propagation throughout the microstructure, as predicted in studies by Wang et al. (2018) and Yuan et al. (2014)

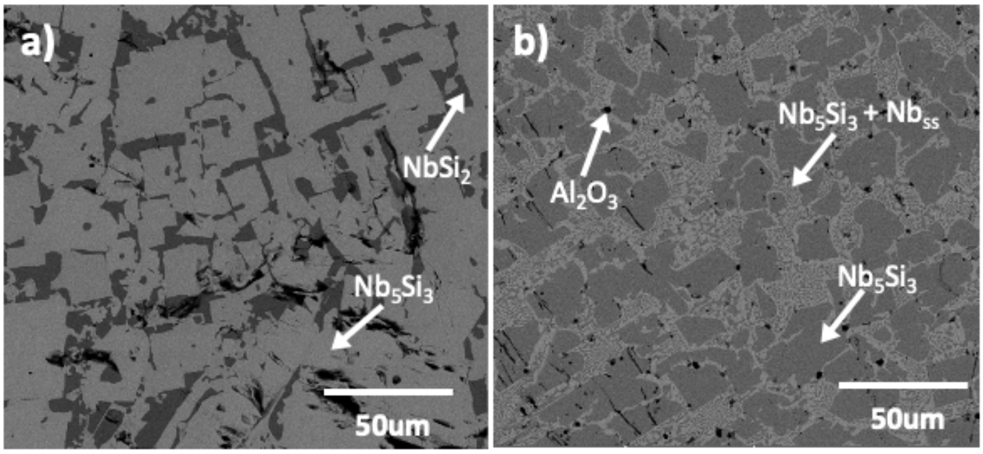

Figure 9 - Top layer of the multilayer built in air with the Nb37wt%Si mixture (a) and the Nb26wt%Si11wt%Al mixture.

Although the intrinsic brittleness of intermetallic compounds is due to their ordered crystal structure, large elemental cell size, and restricted slip system (Kim et al. 2001), there are differences between these compounds. With higher shear stress, elastic modulus, and less fracture toughness compared to Nb_5Si_3, $NbSi_2$ is also the most brittle niobium silicide (PAPADIMITRIOU et al., 2014). $NbSi_2$ cracks are commonly found in arc-melt microstructures due to the residual stresses related to the solidification step (Zhang et al., 2005).

Processing in an argon environment strongly impacted microstructure, particularly the binary powder mixture favored the formation of the phases $NbSi_2$ and Nb_5Si_3, Fig. 10 (a), which resulted in a reduced number of cracks. A lower density of small transverse cracks across Nb_5Si_3 compared to the microstructure built in air evidence the effectiveness of the controlled atmosphere in reducing the formation of nano-oxides, preventing further volume expansion. Processing the ternary mixture in argon, Fig. 10 (b), contributed to reduces the amount of Al_2O_3 particles, however, the oxide still forms in this condition. It suggests that aluminum powder add oxygen to the molten pool. The absence of cracks contributes to the soundness of the ternary multilayer also improves when processing in controlled atmosphere.

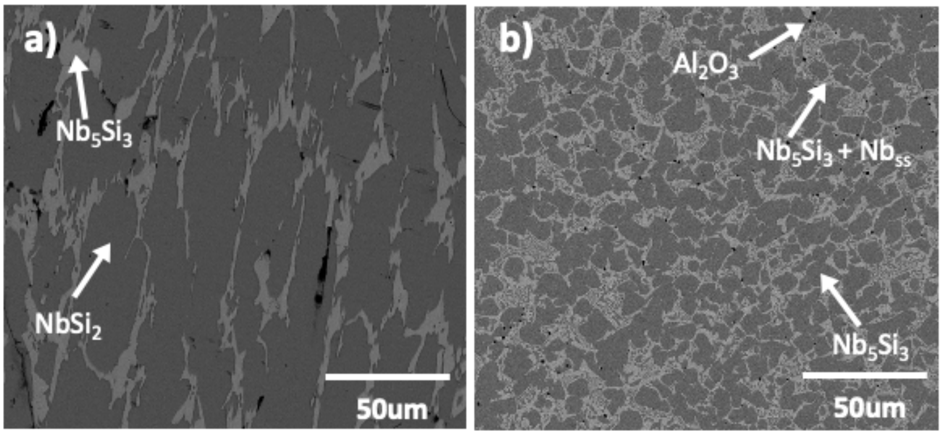

Figure 10 - Top layer of the multilayer built in argon with the Nb37wt%Si mixture (a) and the Nb26wt%Si11wt%Al mixture.

4. CONCLUSIONS

Under the conditions used in this study of the fabricability of Nb silicides multilayers by the deposition of Nb+Si based powder mixtures by Plasma transferred arc, it is possible to conclude that:

- "In-situ" synthesis of silicides was successfully achieved for the tested powder mixtures composition
- Chemical composition of the powder mixtures impacts the wetting angle and as a consequence the multilayers processing parameters
- Oxygen availability during processing strongly affects phase distribution and the soundness of multilayers.

5. ACKNOWLEDGEMENTS

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