

COB-2023-1584
**FABRICATION OF Nb-Si-Al COMPONENTS BY ADDITIVE
MANUFACTURING TECHNIQUES**

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Abstract. *Nb based alloys are considered the most appropriate to meet extreme environmental requirements replacing Nickel superalloys when they no longer respond accordingly. Although the fabrication of Niobium alloys is challenging, Additive Manufacturing processing techniques allow to process advanced materials by in-situ synthesis of Nb alloys simultaneously with the construction of the component. Laser Powder Bed Fusion (LPBF) is a widely used, associated with a high geometry resolution and the high thermal gradients that account for a fine microstructure. LPBF contrast with Arc-DED additive techniques that offer a larger productivity and coarser microstructures due to the lower thermal gradients imposed during the deposition of each layer. Little is known about the processing of Niobium alloys by additive techniques, as well as the properties of these additive parts. This investigation takes an important step to process sound Niobium alloys containing high hardness low toughness silicide compounds as multilayers, taking advantage of the in-situ synthesis of alloys during the processing of multilayers. The LPBF “in-situ” synthesis of the Nb₄₇Si₁₀Al powder mixture, was compromised by the fast solidification rate indicating that low thermal gradients are required to successfully induce in-situ synthesis of Nb silicides. To achieve lower thermal gradients, the Plasma Transferred Arc Directed Energy Deposition (PTA-DED) process was successfully chosen to obtain in-situ synthesis of Nb-based alloys during the deposition of an elemental powder mixture. Multilayers were processed and the impact of multiple thermal cycles in the microstructure of the Nb silicide walls was discussed.*

Keywords: *Additive manufacturing, Laser powder bed fusion, Plasma Transferred Arc, Niobium alloys, Refractory material*

1. INTRODUCTION

Nb-Si based alloys are one of the most considered candidates to build the next generation high temperature equipment such as land-based gas turbines and air-craft engines. The increased need for thermal efficiency of high-temperature equipment, together with a more severe environmental legislation that imposes carbon emission reduction, has fueled the search for materials that can withstand very high-temperature conditions. It brings back the refractory alloys as interesting materials.

New manufacturing technologies enhanced with new software and computational methods, are opening new possibilities for refractory metals. Refractory metals can be manufactured by arc-cast, powder metallurgy, spark plasma sintering, chemical vapor deposition, and hot isostatic pressure. However, when there is a need to manufacture high hardness components with complex structures, these previously mentioned technologies are limited.

The development of Additive Manufacturing (AM) techniques, together with new software and computational methods, make the manufacture of Niobium based refractory components increasingly possible (Ghosh & Olson, 2007). Powder Additive Technologies might allow in-situ synthesis of complex alloys during the deposition of elemental powder mixtures. Directed Energy Deposition Additive processes also allow to gradually change composition layer by layer to build a functionally graded component. Furthermore, the layer-by-layer approach offers a toolless manufacturing process and high material usage efficiency, making the competitiveness of his technology very attractive. Few studies have been published on AM of Niobium and Niobium alloys, but results confirmed AM as a promising approach for processing these materials (Allen et al., 2019; Cardozo et al., 2023; Cardozo & D'Oliveira, 2022; Guo et al., 2018; Philips et al., 2020). In addition to facilitating the manufacture of Nb-Si alloys, additive processes can provide components with improved mechanical properties. (Li et al., 2019) observed the fracture toughness of different Nb-16Si based alloys prepared by different processing techniques and highlighted that the fracture toughness of Nb-22Ti-16Si-2Hf-2Al-2Cr alloy prepared by arc melting is higher than prepared by reactive hot press sintering. Furthermore, higher fracture toughness was achieved by the alloy Nb-22Ti-16Si-5Zr processed by Laser Direct Deposition Metal Additive Manufacturing, called by the author as Laser Solid Forming (LSF).

This study will explore the Nb₄₇Si₂₀Al (at%) alloy processed with powder bed fusion and directed energy deposition additive techniques, namely Laser Powder Bed Fusion (LPBF) and Powder Plasma Transferred Arc (PTA-DED). The potential of performing in-situ synthesis of Nb-Si compounds by each processing technique was assessed.

To investigate Nb-Si based alloy processed by AM, two approaches were tested in this study. As a starting point, a more frequently used technique was explored to process elemental powder mixtures. The thin layer thickness, multiple thermal cycles, and the high energy density of LPBF process make it an attractive tool for the processing of the refractory materials. However, further analysis induced the use of PTA-DED to process Nb based powder mixtures. Both approaches contribute to the state-of-the-art knowledge on Nb and Nb based alloys processed by AM.

2. MATERIALS AND METHODS

Commercially pure niobium, silicon and aluminum elemental powders with irregular morphology, Figure 1, were used to prepare the powder mixture with the composition Nb₄₇Si₂₀Al (at%) using rolling bottles during 6h. Before deposition, the mixtures were kept protected against humidity to prevent the influence of ambient humidity on the flowability.

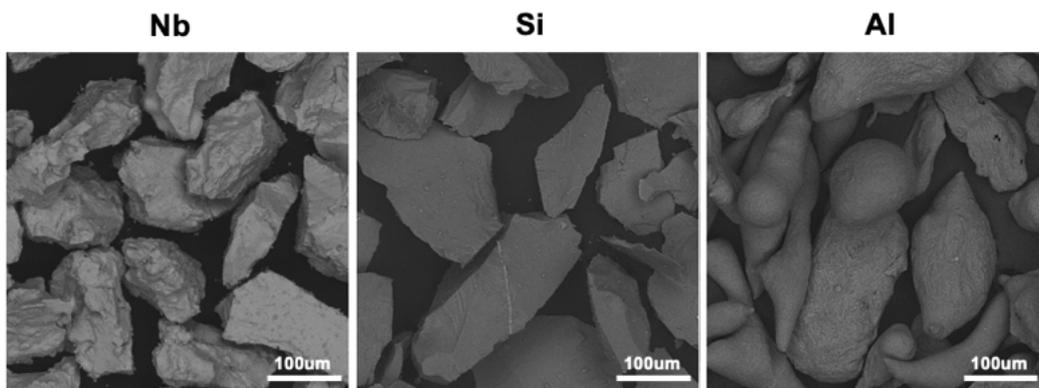


Figure 1. Elemental powders used to produce the mixtures for PTA-DED process.

To assess Niobium-silicide based alloys processed by AM, in-situ synthesis procedures during processing of the mixture Nb₄₇Si₂₀Al (at%) were used to obtain the alloy both by LPBF and PTA-DED, LPBF processing was carried out with the processing parameters described on Table 1, and the processing parameters used for PTA-DED are described on Table 2. The PTA-DED process was performed both into a camera with controlled argon atmosphere, and also with only the argon shield from the machine torch (ambient processing) in order to understand the effectiveness of the shielding system in mitigating the oxygen solubility in melting pool.

Table 1. Processing parameters used in LPBF process.

LPBF	
Power	200 – 225 W
Speed	1900 – 2250 mm/s
Hatch spacing	0,05 mm
Thickness	30 µm
Island size	5x5 mm
Variation between layers	76°

Table 2. Processing parameters used in PTA-DED process.

PTA-DED	
Average Current	100 A
Speed	0,5 mm/s
Feeding rate	0,7 g/min
Feeding gas flow	0,8 l/min
Plasma gas flow	1,8 l/min
Shield gas flow	15 l/min
Nozzle size	3,2 mm
Stand of distance	10 mm
Feeding gas flow	4 mm

Samples were cut from the cross section of the multilayers builds, mounted, ground, and polished with activated oxide polishing suspension. The microstructure was characterized using Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) mapping.

3. RESULTS

Processing Nb₄₇Si₂₀Al elemental powder mixtures with LPBF provided challenges associated with the *in-situ* synthesis of compounds together with the already mentioned irregular morphology of powders. Builds processed with the final window are shown in Figure 2. Compared to pure Nb, Niobium-silicide-based cubes show poor surface finishing, with accentuated roughness, suggesting that the melting of the powder mixture might have been compromised.

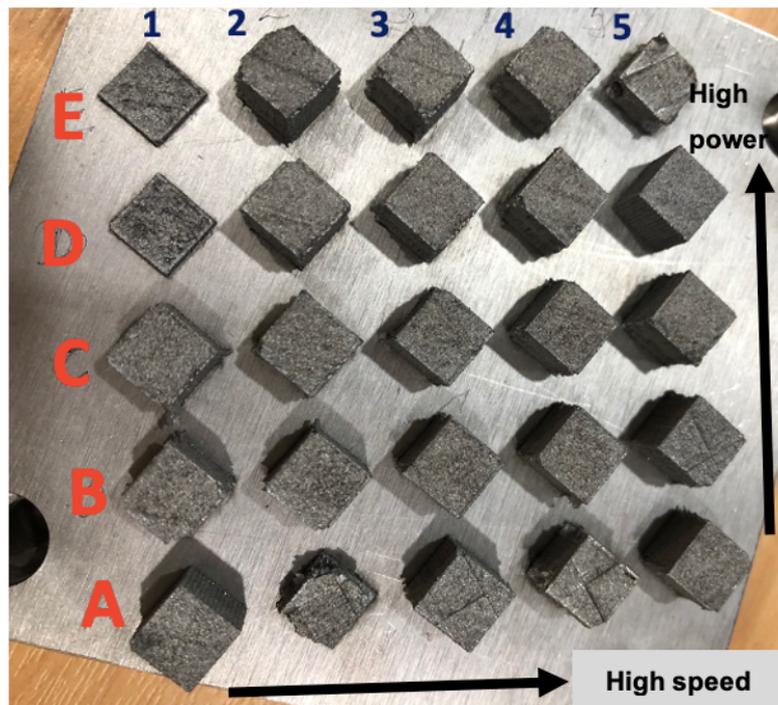


Figure 2. LPBF Processing window for the Nb₄₇Si₁₀Al powder mixture.

Pores, unmelted particles and a non-homogeneous microstructure, Figure 3 (a), are present in the builds confirming that the range of energy density was not sufficient to complete the *in-situ* synthesis of silicides and to homogenize the microstructure. Cracks are also present, Figure 3 (b), a consequence of low toughness of Nb silicides that cannot accommodate the stresses due to the fast solidification.

The high hardness of builds, 647 ± 309 HV, suggests that the synthesis of silicide compounds occurs but the large dispersion is accounted for by an incomplete synthesis that leads to the heterogeneity of builds. The elements distributed heterogeneously over the melting pool, segregating, and spreading in swirl-like patterns potentially caused by convection inside the melt pool, Figure 3 (b).

Results allow to raise the hypothesis that the synthesis of silicides requires a longer interaction between powders while exposed to a large energy density and that, for this technique to achieve a homogeneous microstructure, a pre-alloyed and spherical Nb₄₇Si₂₀Al powder, as typically used in L-PBF might be required. However, literature shows that, even using

pre-alloyed spherical powders and higher energy densities, the synthesis of a Nb-based alloy by L-PBF is still a challenge. (Guo et al., 2018) reported similar behavior processing single layers with pre-alloyed powders of Nb₃₇Ti₁₃Cr₂Al₁Si by L-PBF, using higher energy densities ($v=200\text{mm/s}$, $P=380\text{W}$, $t=80\mu\text{m}$, $h=0,05\text{mm}$).

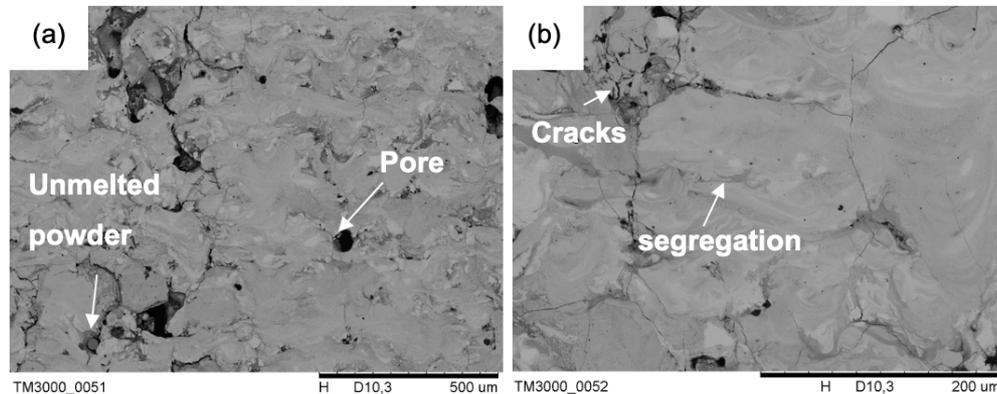


Figure 3. Nonhomogeneous microstructures of the cubes fabricated by LPBF with the Nb₄₇Si₁₀Al powder mixture.

Furthermore, in spite of the larger number of heating cycles that remelt and reheated previous layers, the fast-scanning speeds of L-PBF processing can be accounted for the observed incomplete synthesis of silicide compounds. Hence, build of Nb silicides obtained by in-situ synthesis might be successfully achieved by a Direct Energy Deposition technique that gives a reduced thermal gradient and longer interaction between powders.

Considering these results, in particular the impact of the fast solidification rates in laser processing, Plasma Transferred Arc (PTA-DED) appears as an advantageous technique for processing builds of these materials. Besides the less severe solidification rates, this technique also allows to manipulate the composition of the alloy layer by layer. To assess the hypothesis that lower thermal gradient allows for the successful processing Nb silicides, PTA-DED was used for the deposition of multilayers.

The complete in-situ synthesis of intermetallic compounds successfully occurred during deposition of the ternary NbAlSi powder mixture by PTA-DED, as confirmed by the absence of unmelted particles and the uniformity of the microstructure Figure 4. The solidification structure of multilayers processed in both camera of controlled atmosphere and ambient atmosphere exhibits Nb₅Si₃ dendrites with Al in solid solution, surrounded by an interdendritic eutectic containing Nb_{ss}, Figure 4 (a) and (b) respectively.

The PTA-DED processed multilayers show a small and reduced number of cracks confined within the Nb₅Si₃ dendrites. The ductile eutectic containing Nb_{ss} contributed to mitigate crack propagation throughout the microstructure, as predicted in studies (Wang et al., 2018; Yuan et al., 2014).

The major impact from processing without controlled atmosphere (argon camera) is the larger amount of Al₂O₃ particles (black dots) confirmed by the composition mapping, Figure 4 (c), and the smaller fraction of the Nb_{ss} phase in the interdendritic eutectic. It is interesting to note that, in spite of controlling the oxygen at 53ppm, small oxide particles still form in multilayers processed with the argon camera, suggesting that powder particles might have carried oxygen into the melt pool.

The absence of ternary phases contrasts with the results from solid state processing reported by (Murakami et al., 2001). The formation of alumina and the eventual evaporation of aluminum in the powder mixture during processing may contribute to preventing the formation of the ternary phase.

Phase distribution is similar in both multilayers and the observed differences are a consequence of oxygen and aluminum content in solution in the melt pool. Al trapped in the Al₂O₃ particles depletes the composition of the solidifying melt pool, as shown by the difference in Al content in phases of builds processed in ambient conditions and in the argon camera, Table 3. The Al content in Nb_{ss} is observed in both environments but processing in argon resulted in a higher Al content in Nb_{ss}, in agreement with the reduced oxide particles in the microstructure. The observed phase distribution agrees with predictions from the phase diagram considering each layer composition.

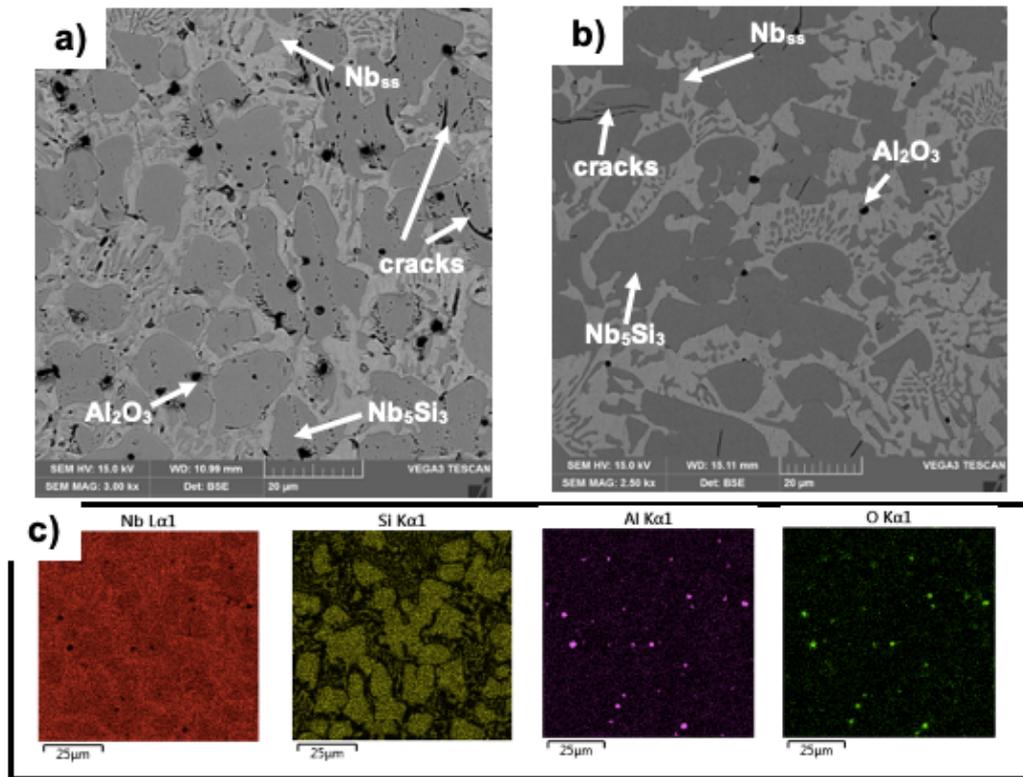


Figure 4. Bottom layer of the multilayer processed in air (a); bottom layer of the multilayer processed in a camera with an argon atmosphere (b) and the EDS composition map (c) of the multilayer processed under ambient processing.

Table 3. Average content of niobium, silicon, and aluminum in each phase of the ternary multilayer processed in ambient conditions (T-air) and the ternary multilayer processed in an argon camera (T-argon), accessed by EDS analysis.

		T-air			T-argon		
		Average composition [at%]			Average composition [at%]		
		Nb	Si	Al	Nb	Si	Al
Powder Mixture		33	47	20	33	47	20
Interdendritic	Nb _{ss}	91.35±0.4	1.48±0.2	7.15±0.5	87.50±0.9	2.70±1.1	9.73±0.9
	Nb ₅ Si ₃	70.33±4.1	24.10±4.8	5.55±0.9	68.58±2.2	23.85±2.5	7.58±0.3
Dendrite	Nb ₅ Si ₃	64.30±0.2	32.35±0.7	3.35±0.5	64.38±0.3	29.55±1.3	6.10±1

4. CONCLUSIONS

Data showed LPBF is not adequate to process Nb silicide alloys by *in-situ* synthesis, inducing the selection of a DED technique that allows for the use of powder mixtures, PTA-DED, to assess additive processing of Nb silicide alloys. This procedure allowed for a better understanding of the impact of alloying elements and of the processing environment on the processability of Nb silicide-based alloys.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by CAPES and CNPq and wish to thank CBMM for supplying the niobium powders and substrate. We also thank Professor Moataz Attallah for providing lab floor and equipment to process the LPBF coupons.

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