MICROSTRUCTURE EVOLUTION OF THE Nb-18Si-24Ti-5Cr-5Al-2Mo ALLOY PRODUCED VIA LASER ADDITIVE MANUFACTURING

FEITOSA Leandro, ALLEN Adam, DOUGLAS Andrew, QIAN Huan, DONG Hongbiao

University of Leicester, Department of Engineering, Leicester, England, United Kingdom, EU

Abstract

Niobium silicide based alloys with composition Nb-18Si-24Ti-5Cr-5Al-2Mo were prepared via laser additive manufacturing and analyzed with back-scattered scanning electron microscope and energy-dispersive X-ray spectroscopy in order to evaluate the solidification sequence during freezing and the microstructure evolution during post heat treatment process. Following primary formation of Nb_5Si_3, and eutectic reaction L → Nb_5Si_3 + Nb_{ss}, takes place and Nb_3Si phase is suppressed, deviating from the equilibrium predictions. Due to high Ti concentration, a second Ti-rich Nb_5Si_3 phase is formed.

After heat treatment at 1200 °C, coarsening of phases has been observed with a decreasing of the Ti-rich Nb_5Si_3 phase. A new formation of a Ti_{ss} solution phase has occurred in small volume fraction, which is related to the local super-saturation and high temperature diffusion.

A better understanding of the microstructure evolution was therefore required in order to follow the formation and change of phases from the solidification to the heat treatment stages. This study was focuses on the analysis of the solidification behavior of the multi-component Nb-18Si-24Ti-5Cr-5Al-2Mo alloy under rapid freezing produced via laser additive manufacturing processing posteriorly heat treated at 1200 °C.

Keywords: Niobium-silicide alloys, microstructure evolution, laser additive manufacturing, rapid freezing

1. INTRODUCTION

Niobium silicide-based alloys have a potential application in gas turbine blades, promising significant improvements when compared to Ni-based alloys. This is due to the higher temperature capability that they present and significant lower density and good mechanical properties, conferred by the presence of reinforcing ceramic phases, such as Nb_5Si_3 and/or Nb_3Si, embedded in a ductile solid solution phase, Nb_{ss}. The combination of these properties would allow the manufacturing of lighter engines able to run at higher temperatures, increasing their efficiency [1, 2]

A typical Nb-silicide alloy is composed of a Nb solid solution, defined as Nb_{ss} containing brittle silicide phases with different structures, such as α, β, γ-M_5Si_3 and/or M_3Si [3, 4]. Other important phase can be present when Cr is added, forming Cr_2Nb, the Laves phase (C14 or C15), which improves the oxidation behavior of these alloys when present in a volume fraction less than 10 at.% Cr [5, 6].

The addition of alloying elements such as Al, Ti, Cr, Hf, V and Mo seeks a balance of properties to produce a composite useful in applications in high temperature [7-9]. Additions of Al and Cr improve the fracture toughness and the oxidation behavior of these alloys, since it reduces the oxygen diffusivity and due to the formation of a protective Al-oxide layer and Laves phase in small contents [10, 11]. The use Ti increases the kinetics of transformation from Nb_3Si silicide to the more stable Nb_5Si_3, and it coarsens the Nb particles, increasing the ductility of the alloy and the fracture toughness by deflection of cracks [12, 13]. Additions of V and Mo control the formation of the Nb_5Si_3 silicide phase, increasing the yield strength at room temperature. Additions Hf affect the fracture toughness, room strength and the oxidation behavior, which requires small contents, and it also produces HfO_2 particles, cleaning the alloy from oxygen inclusions and increasing its hardness [5, 14].

High additions of Ti affect the binary Nb-Si system in a large scale, and therefore a ternary Nb-Si-Ti system is analyzed instead, also exploring the effect of other elements in the microstructure [15, 16]. The liquidus projection for this system was first built by Bewlay et al. [17] when studying Nb-rich and Ti-rich ternary Nb-Si-Ti alloys, and later thermodynamically assessed by Jing et al. [18].

However, given the possibility of compositions and elemental additions, a full understanding of the microstructure evolution is needed, based on the solidification path predicted. In this work, the liquidus projection for the ternary Nb-Si-Ti system will be presented as basis for the study of the solidification path of the alloys developed, following by a closer analysis of how the microstructure evolved from the as-formed samples before and after heat treatment at 1200 °C.

2. EXPERIMENTAL

The multi-component Nb-Si-Ti samples were prepared using a laser additive manufacturing method (LAM), which comprises of a laser beam, responsible for melting the powder mixture introduced into a solid substrate by a feeder. Through CAD construction and CNC technology, the beam can be moved freely in space to build complex pieces in a sequence of layers. **Figure 1** shows the schematic for such technique.

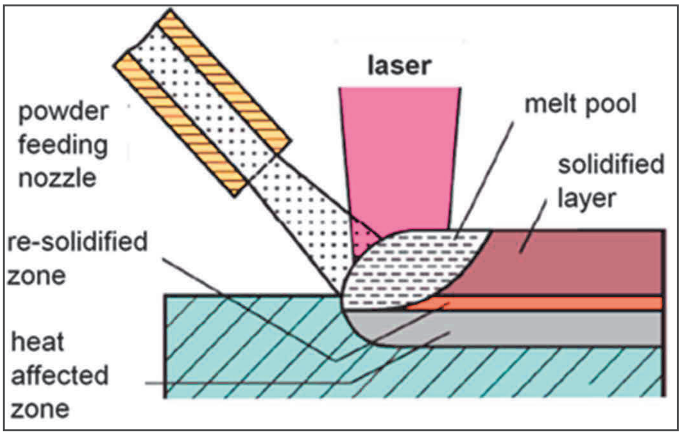

Figure 1 Schematic of the LAM processing method.

The main advantages of this process are the possibility of obtaining complex shapes, processing near net-shape components without using expensive and inert mold, the good mix of the elements, which reduce the waste of material and less micro-segregation. Disadvantages are the relatively poor dimension tolerance comparing with the powder-base method and control of scanning speed to avoid materials loss. It was noted that increasing the speed scan increases the efficiency [19, 20].

The parameters used during the preparation and forming of the materials are detailed in **Table 1**. The nozzle was fed with a pre-mixed powder of the elements needed to produce the compositions aimed. With a laser melting the powder into a Ti substrate, a protective gas was used at all times to prevent oxidation on the molten pool.

Table 1 Parameters used for the LAM equipment during processing

Parameter	Value
Laser Power	3.0 kW
Spot size	6.0 mm
Powder flow rate	6.0 $l \cdot min^{-1}$
Scanning Speed	600 $mm \cdot min^{-1}$

The alloys prepared by LAM were heat treated at 1200 °C, to provide comparison and to observe possible formation or dissolution of phases for the given treatment, X-ray diffraction (XRD) was required to confirm the phases present in each case.

The final microstructures of the samples obtained before and after heat treatment were characterized using a Philips XL 30 scanning electron microscope (SEM), equipped with energy-disperse X-ray spectroscopy analysis (EDS), with which phases were identified.

3. RESULTS AND DISCUSSIONS

The calculated liquidus projection for the ternary Nb-Si-Ti system is presented in **Figure 2**, with the average measured composition superimposed. The solidification sequence can then be obtained, which shows the silicide Nb_5Si_3 as the primary phase closely to the peritectic valley, and the sequence of freezing is described as follows; L → Nb_{ss}, L → Nb_{ss} + Nb_5Si_3, L → Nb_5Si_3.

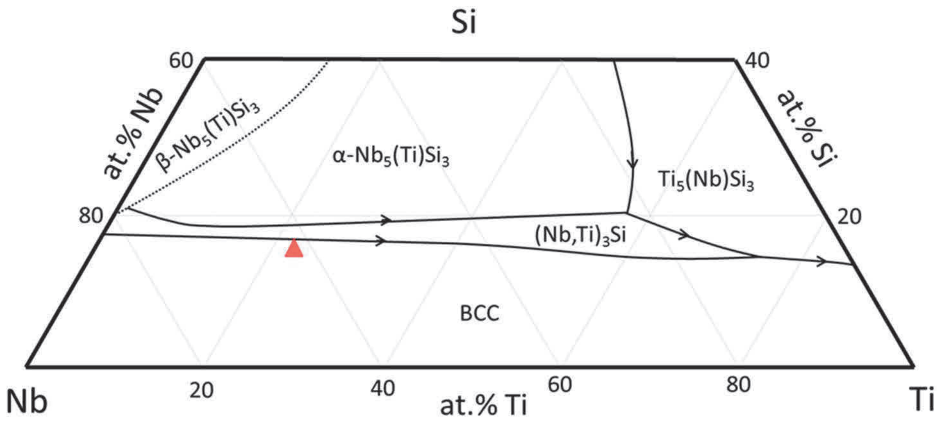

Figure 2 Calculated liquidus projection for the ternary Nb-Si-Ti system [5]

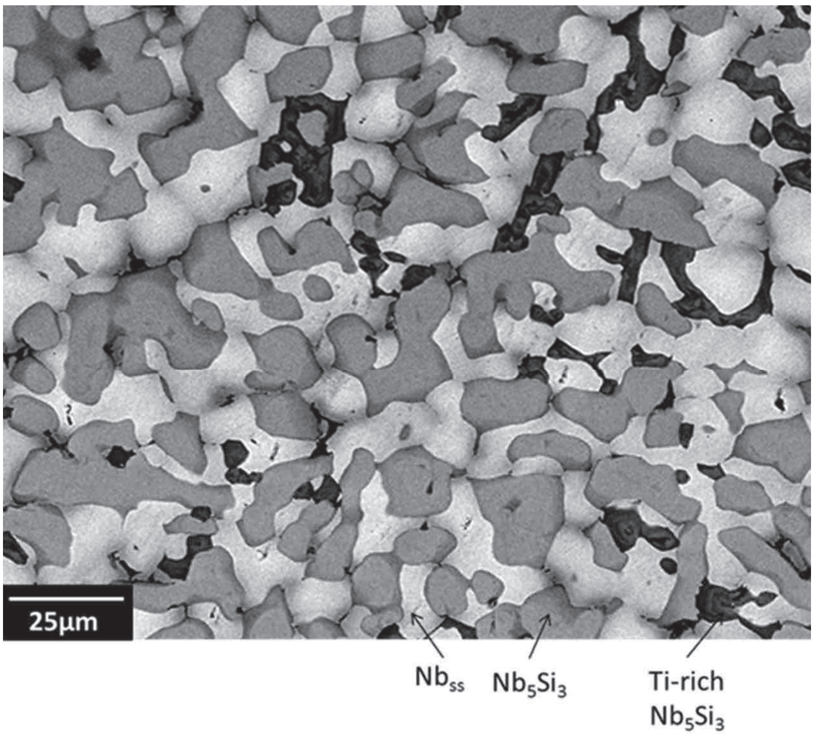

Figure 3 Microstructure of as-formed Nb-18Si-24Ti-5Cr-5Al-2Mo alloy

The back-scattered electron image (BEI) of the as-formed Nb-18Si-24Ti-5Cr-5Al-2Mo sample microstructure is presented in **Figure 3**. A primary dendritic structure of Nb_{ss} is formed followed by a eutectic pattern of Nb_{ss} + Nb_5Si_3 throughout the sample, and a third formation of a dark Ti-rich Nb_5Si_3 phase, which is formed in the last stage of solidification, is observed in the eutectic channels. A layer richer in Ti is formed at the boundaries of the Nb_{ss} and Nb_5Si_3 phases.

After EDS and XRD analysis (**Figure 4**), it can be confirmed that the composition of the dark phase to be a Ti-rich Nb_5Si_3 phase, which is due to the large extend of the Nb_5Si_3 phase varying Ti contents in the diagram. An initial observation of this was assessed when comparing the composition of these phases with that tested by Li et al. [16], where it can be seen that they can present the same phases with large differences of Ti content, given by the large miscibility gap, which is also influenced by the rapid solidification rate proportioned by this processing method.

With a rapid decreasing of temperature, there is a drop in Ti solubility for the silicide, which characterizes a rejection of solute to the liquid that solidifies as a Ti-rich silicide. This is evidenced in the microstructure pattern observed, with the dark silicide phase forming adjacent to the eutectic cellules.

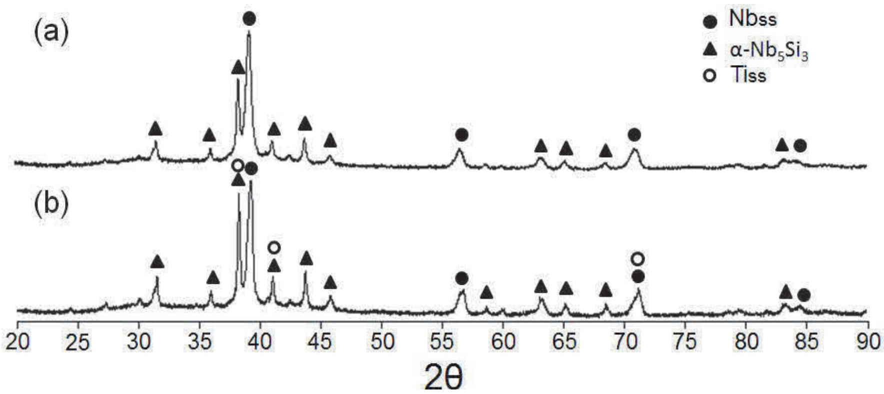

Figure 4 X-ray diffraction for (a) as formed and (b) heat treated sample

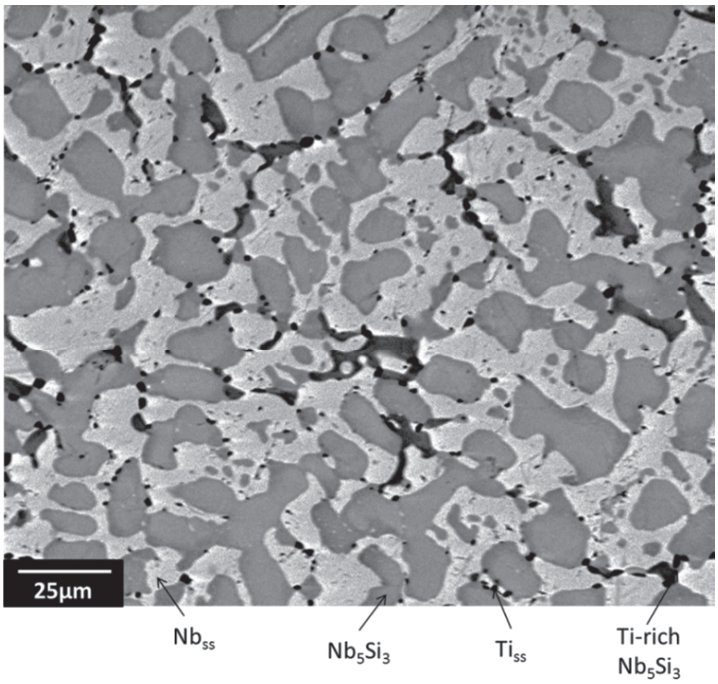

Figure 5 Microstructure of Nb-18Si-24Ti-5Cr-5Al sample after heat treatment at 1200 °C

The BEI for the heat treated Nb-18Si-24Ti-5Cr-5Al sample is presented in **Figure 5**, where a relative coarsening of the Nb_{ss} and the Nb_5Si_3 phases can be observed, with a decrease in contrast of the Ti-rich Nb_5Si_3 phase, showing that there is a reduced of Ti. This is observed to occur due to the diffusion that equilibrates the unbalanced solute concentration. A new phase with small volume fraction of a punctual-like growth has taken place forming a Ti-rich solid solution, Ti_{ss}.

The diffusion of Ti is followed by a restriction of the coarsening of Ti_{ss} phase, which is due to the decreasing temperature from the cooling stage, forming phases of small volume, which relates to shorter distances for the Ti solute to diffuse. The formation of a new solid solution phase during heat treatment has also been observed by Tewari et al. [21], when analyzing low temperature aging of multi-component Nb-Si-Ti alloys. A similar approach can be used of that observed in Ti-X alloys [22], where it has been highlighted that the formation of a new solid solution phase can follow the super-saturation of parts of the original silicide, namely Nb_{ss} saturating in Ti which then relives its saturation into forming a more stable local equilibrium phase, when a spinodal decomposition is observed [23].

4. CONCLUSION

1) High Ti addition promotes and stabilizes Nb_5Si_3 silicide phase with suppression of Nb_3Si phase.
2) The formation of a new Ti-rich Nb_5Si_3 silicide phase, followed a large miscibility gap, is conferred due to the rejection of solute to the liquid and decrease of the solute solubility with temperature.
3) Local segregation and super-saturation led to the formation of a Ti_{ss} phase following diffusion of Ti into a more stable and homogeneous composition.

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