Solidification of niobium-silicide-based alloys during laser additive manufacturing process

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Abstract. Niobium silicide-based composites, in the application of gas turbine blades, promise significant efficiency improvements compared to current Ni-based alloys. The higher temperature capability would allow the engine to run at a higher temperature than that of current alloys, increasing engine efficiency. Nb-Si based composites possess a lower density, due to the presence of ceramic phases such as Nb₅Si₃ and/or Nb₂Si. This would reduce the weight of the rotating blades. However, improvements in certain properties, such as room temperature toughness and oxidation resistance are needed.

This study focuses on the manufacturability aspect of the powder feeding laser additive manufacturing (LAM) process to engineering Nb-Si based alloy samples. LAM has the advantage of forming near-net shapes without the use of expensive cores and moulds for the reactive Nb-Si melt. Fine microstructure and even chemical composition distribution with reduced macro-segregation are obtained. With the use of power feeding system, new Nb-Si based alloys are LAMed with varying atomic composition. Microstructures of the LAMed alloys will be presented, and the relationship between the microstructure and the alloy chemistry will be reported.

Keywords: microstructure evolution; laser additive manufacturing; niobium-silicides; rapid freezing; diffusion.

1. Introduction

Niobium silicide-based composites, in the application of gas turbine blades, promise significant efficiency improvements compared to current Ni-based alloys [1]. Higher temperature capability would allow engines to run at higher temperatures, increasing their efficiency [2]. These composites also possess lower density further increasing engine efficiency [3]. The high promise of Nb-silicide based alloys combined with the manufacturing processes based on AM methods have been proven to be highly innovative, as it opens a new window of opportunities for efficiency, the reduction of energy consumption and the waste of raw materials [4].

Additions of alloying elements such as Al, Ti, Cr, Hf, V and Mo into the composition of Nb-silicide alloys seeks a balance of properties to produce a composite useful in applications at high temperatures [5]. Al and Cr are used to improve the oxidation behaviour by reducing oxygen diffusivity and forming a protective Al-oxide layer and Laves phase [6]. Ti can increase the kinetics of transformation from Nb₅Si to Nb₃Si₃, and it increases the fracture toughness and the ductility of the niobium solid solution [7]. The silicide phase can form as a tetragonal high temperature β-Nb₅Si₃, the tetragonal low temperature α-Nb₃Si [8], or as the metastable hexagonal γ-Nb₂Si₃ silicide. The γ-Nb₂Si₃ is not desirable owing to its creep properties [9]. The Nbₓv can present high concentration of Ti with very low amounts of Si [10]. In relatively large amounts, it pushes the Nb-silicide composites to a ternary system, therefore a fair understanding of the phase equilibria for this is needed [11]. Additions of V and Mo control the
formation of $\alpha$-Nb$_5$Si$_3$ phase, which increases the yield strength at room temperature. Additions of Hf improve the fracture toughness, room temperature strength and the oxidation behaviour [12].

2. Experimental

Nb-18Si-24Ti-5Cr-5Al-2Mo (2Mo) and Nb-18Si-24Ti-5Cr-5Al-2Mo-5Zr-0.4Y (5Zr) bars were prepared using a LAM method. The laser process requires a substrate, in this case titanium. A focused laser beam is aimed onto the substrate to create a molten pool, with a constant flow rate of metallic powder being directed at the beam through a nozzle. A computer numeric control (CNC) motion system assists the movement of the substrate, creating the final piece shape with a computer assisted design (CAD) model. As the substrate moves, the molten pool is dislocated, leaving a rapidly solidified layer behind. Figure 1 shows the schematic for LAM.

![Figure 1 - Schematic of the LAM processing method.](image)

The second step of this process involves the deposition of a following layer of metal on top of the initial layer, creating a wall structure. The repetition of this step is designated to form complex shapes by the movement of the laser beam, which controls the direction of the molten pool, and therefore the design of the shaped part without any mould or die.

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 onto a Ti substrate, a protective argon gas was used at all times to prevent oxidation of the molten pool.

| Parameter            | Value     |
|----------------------|-----------|
| Laser power          | 3.0 kW    |
| Laser spot diameter  | 5.0 mm    |
| Powder gas flow rate | 6.0 L/min |
| Scanning speed       | 900 mm/min|

The compositions and microstructures were characterised using an FEI FEG scanning electron microscope (SEM), equipped with energy-disperse X-ray spectroscopy analysis (EDS), with which phases were identified. A Bruker D8 Advance with DaVinci X-ray diffractometer was used to analyse crystal structure.
3. Results and Discussion

3.1. 2Mo

The as-formed microstructures are shown in Figure 2. 2Mo appeared to exhibit a three-phase microstructure with a Nb5Si3 primary phase, a Nbss phase and a further Ti-rich Nb5Si3 phase. The elemental composition of the phases and volume fraction is shown in Table 2.

Table 2 - Phase elemental composition (at%) and volume fraction for 2Mo

| Phase          | Nb    | Si    | Ti    | Al   | Cr   | Mo    | Volume Fraction (%) |
|----------------|-------|-------|-------|------|------|-------|---------------------|
| Nbss           | 46.39 | 6.65  | 28.36 | 6.98 | 8.82 | 2.81  | 33.73               |
| γ-Nb5Si3       | 45.42 | 32.35 | 17.31 | 3.03 | 1.00 | 0.88  | 35.38               |
| Ti rich γ-Nb5Si3 | 34.85 | 28.30 | 28.84 | 4.45 | 2.76 | 0.79  | 30.89               |

XRD analysis using MAUD [13], shown in Figure 3, suggest that the only silicide present was the γ-Nb5Si3 crystal structure, therefore indicating that the Ti-rich Nb5Si3 phase was also of the γ crystal structure. A similar alloy was produced by Geng et al [16] using vacuum arc remelting but produced a microstructure with β-Nb5Si3 and another silicide Nb3Si. It is thought that the relatively rapid cooling rate of additive manufacture compared to vacuum arc remelting alters the solidification path, bypassing the formation of Nb3Si. It is also known that high concentration of Ti can include the formation of Ti5Si3 [14], which possesses the same crystal structure as γ-Nb5Si3. It is known that high Hf content can promote the formation of the γ-silicide [10], and Ti and Hf are in the same column of the periodic table, indicating similar properties. It is likely therefore that the high Ti content combined with rapid cooling resulted in the formation of the γ-Nb5Si3 rather than the β-Nb5Si3 observed by Geng. The morphology shows a uniform microstructure with smoothed blocks of the primary silicide in a matrix of Nbss. The Ti-rich silicide was dispersed amongst the Nbss. The proposed solidification sequence is as follows:

L \rightarrow γ-Nb5Si3

L \rightarrow Nbss + γ-Nb5Si3 (Ti saturated)

The γ-Nb5Si3 forms first as the liquid cools. This reduces the amount of Si in the liquid and increases the amount of Ti as the primary silicide only contains 17 at.% Ti. As the liquid cools further, the Si depleted liquid begins to form Nbss and further amounts of γ-Nb5Si3. However, the forming Nbss is ejecting Ti as it becomes saturated, resulting in the formation of a Ti-rich Nb5Si3 phase.

3.2. 5Zr

Initially, 5Zr appeared to exhibit a two-phase microstructure of a primary Nb5Si3 phase inside a continuous matrix of Nbss. Closer inspection shows there was still small amounts of Ti-rich Nb5Si3 present but was integrated into the primary γ-Nb5Si3. The elemental composition and volume fraction are shown in Table 3, clearly showing that Zr partitions primarily to the γ-Nb5Si3 phase.
Figure 2 – Backscattered electron images of a) 2Mo and b) 5Zr alloys. Images were captured at the centre of the samples.

Figure 3 – Backscattered electron images of a) 2Mo and b) 5Zr alloys. Images were captured at the centre of the samples.
This also shows a reduced amount of Ti-rich silicide present. MAUD analysis [13], again in Figure 3, shows that the only the γ-Nb₅Si₃ is present. This is logical as the newly introduced Zr is also in the same column of the periodic table as Ti and Hf, which both appear to induce the formation of γ-Nb₅Si₃. It is likely that Zr also induced the formation of γ-Nb₅Si₃.

Table 3 - Phase elemental composition (at%) and volume fraction for 5Zr

| Phase         | Nb   | Si   | Ti   | Al   | Cr   | Mo   | Zr   | Y   | Volume Fraction (%) |
|---------------|------|------|------|------|------|------|------|-----|---------------------|
| Nb₃s          | 58.98| 1.86 | 20.95| 7.85 | 6.52 | 2.64 | 0.81 | 0.42| 51.06               |
| γ-Nb₅Si₃      | 36.61| 32.79| 17.31| 3.69 | 1.00 | 0.08 | 9.49 | 0.14| 48.94               |

The morphology of the microstructure was markedly different. The overall microstructure appeared refined with smaller blocks of silicide phase. In other alloy systems Zr is known to aid grain refinement by creating nucleation sites [15]. The silicide blocks were more angular and exhibited a wide variety of shapes including ‘U’ and ‘H’ shapes. Angular shapes are often the result of more brittle phases, indicating the addition of Zr has reduced the ductility of the silicide. Areas of eutectic Nb₃s/Nb₅Si₃ were present near the larger of the silicide blocks. The Ti-rich silicide only appears to be present on the edges of the primary silicide and not through-out the Nb₃s matrix as with 2Mo alloy. These occurrences are explained in proposed solidification sequence:

L → γ-Nb₅Si₃
L → Nb₃s + γ-Nb₅Si₃
L → Nb₃s + γ-Nb₅Si₃ eutectic

As with the 2Mo alloy, the first phase to solidify is the primary γ-Nb₅Si₃. The remaining liquid is less saturated in Ti as the Zr partitions preferably to the γ-Nb₅Si₃ at the expense of Nb, resulting in more Nb in the Nb₃s. A higher density of grains are formed thanks to the Zr additions forming more nucleation sites. As the liquid cools further Nb₃s and γ-Nb₅Si₃ start to form. With a reduction in the amount of Nb present you would expect the equilibrium to shift away from the eutectic. However, it appears the addition of Zr shifts the system towards the equilibrium and once the liquid is cooled sufficiently eutectic Nb₃s/γ-Nb₅Si₃ forms.

4. Conclusions

(1) Proposed reaction sequences for the 2Mo and 5Zr alloys both show that the γ-Nb₅Si₃ phase forms initially. This is followed by Nb₃s/Ti-rich γ-Nb₅Si₃ for 2Mo and by Nb₃s/γ-Nb₅Si₃ for 5Zr with a small amount of eutectic forming.

(2) γ-Nb₅Si₃ was formed rather than other crystal structures for both 2Mo and 5Zr as Ti and/or Zr content and rapid cooling drive the formation of the hexagonal crystal form.

(3) Adding 5 at% Zr at the expense of Nb appears to have refined the resulting microstructure. This is due to Zr forming more nucleation sites. Zr has also moved the system closer to the Nb₃s/Nb₅Si₃ eutectic, with eutectic formations observed near the larger γ-Nb₅Si₃ blocks. Finally, Zr appears to have made the γ-Nb₅Si₃ blocks more angular in shape. This is likely due to Zr decreasing the ductility of the silicide.
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