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Abstract. Nb-base refractory intermetallic materials have potential interest for high temperature applications thanks to their low density and high temperature strength. While advanced intermetallics in monolithic form have limited prospects for providing the required balance of properties for use at high temperatures, two-phase or multicomponent intermetallic systems composed of a ductile, Nb-base refractory phase in equilibrium with one or more silicide intermetallics show promise for further development as structural materials. In the present paper, Nb-base refractory alloys based on Nb-35Ti-15Al (at.%) were doped with small amount of Si (1 and 2 at% of silicon) addition to improve its high temperature strength by keeping an acceptable ductility at room temperature. The samples were prepared by arc-melting starting from pure elements (99.99%). The silicon addition effects on the microstructural features were investigated by using X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) techniques. Its effects on the mechanical properties were assessed by compression tests at ambient and high temperatures. Compression tests show the beneficial effect of the Si addition on strength.

1. Introduction

Since 1980's, there has been significant research into the exploration of intermetallic alloy systems capable of operation at high temperatures. While the intermetallic systems are known for their exceptional strength and creep resistance at elevated temperatures, they are also known for their brittleness at low temperatures. Numerous investigations have been conducted on Nb-rich alloys related to the phase equilibria between the β_0 (B2) and Nb_3Al (δ, A15) phases [1-6], as well as the mechanical properties of these alloys [7-14]. One of the alloy development strategy was to associate Nb_3Al phase in a Nb_{ss} (B2 structure type) ductile matrix in order to improve the fracture toughness of the Nb_3Al phase at low temperature. However, this alloy system leads to an appreciable decrease in strength at high temperature [15]. Therefore, further studies are needed to increase the high temperature strength in Nb_{ss} as well as Nb_3Al by means of alloying it with element such as Si, Hf or Zr.

In the present study, the effects of alloying Nb_{ss}/Nb_3Al with a low amount of silicon were examined in three different cast alloys (0at.%Si, 1at.%Si and 2at.%Si). The silicon addition effects on the microstructural features were investigated by using X- Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques. Its effects on the mechanical properties were assessed by compression tests at ambient and high temperatures.

2. Experiment

60 cm^3 ingots of alloys used in the study were made from high purity Nb (99.99%), Al (99.99%), Ti (99.99%) and Si (99.99%) by vacuum arc-melting in a water-cooled copper hearth and using a

non-consumable tungsten electrode. Each ingot was remelted 4-6 times to ensure complete mixing of the constituents. The chemical compositions of the three alloys are shown in Table 1.

Alloy reference	Ch. Composition	Nb [at.%]	Ti [at.%]	Al [at.%]	Si [at.%]
M1	Nb-34Ti-15Al	51.5	34.7	13.8	-
M2	Nb-33.6Ti-15Al-1Si	50.7	33.8	14.3	1.2
M3	Nb-33.2Ti-15Al-2Si	49.9	33.9	14.1	2.1

Table1- Nominal and actual chemical compositions in at.% of alloys investigated.

Two homogenization treatments were tested on the as-cast ingots: 1400°C for 24h and 1200°C for 50h in an inert atmosphere. Samples were wrapped in Nb foil prior to treatment. Metallographic samples of the cast and heat treated alloys were examined through back-scatter electron imaging (BSE). Energy dispersive spectrometry (EDS) analyses were used to obtain estimation of the chemical composition of areas in the microstructures. Phase identification was performed by X-ray diffraction (XRD). Foils for transmission electron microscopy (TEM) were prepared by using a variable angle Precision Ion Polishing System (PIPS).

Compression tests were conducted at room temperature and under vacuum at 800°C at a strain rate of 10^{-4} s^{-1}.

3. Results & Discussion

3.1. Microstructure and phase analysis

As-cast

The as-cast materials of the three Nb-rich alloys were examined through various techniques to identify the primary solidification regions. All of the three alloys display a dendritic solidification microstructure (Fig. 1a-c). In M2 alloy containing 1at.% of Si, the as-cast microstructure is very similar to M1 alloy (Fig. 1a) and none of silicide was observed (Fig. 1b). Whereas M3 alloy, with 2 at.% of Si, exhibit primary silicide precipitates (black precipitates) (Fig. 1c) mainly located in the interdentritic (Fig. 1d). In each case, the Nb matrix was identified to be the disordered β (bcc) phase through XRD phase identification technique (Fig. 2).

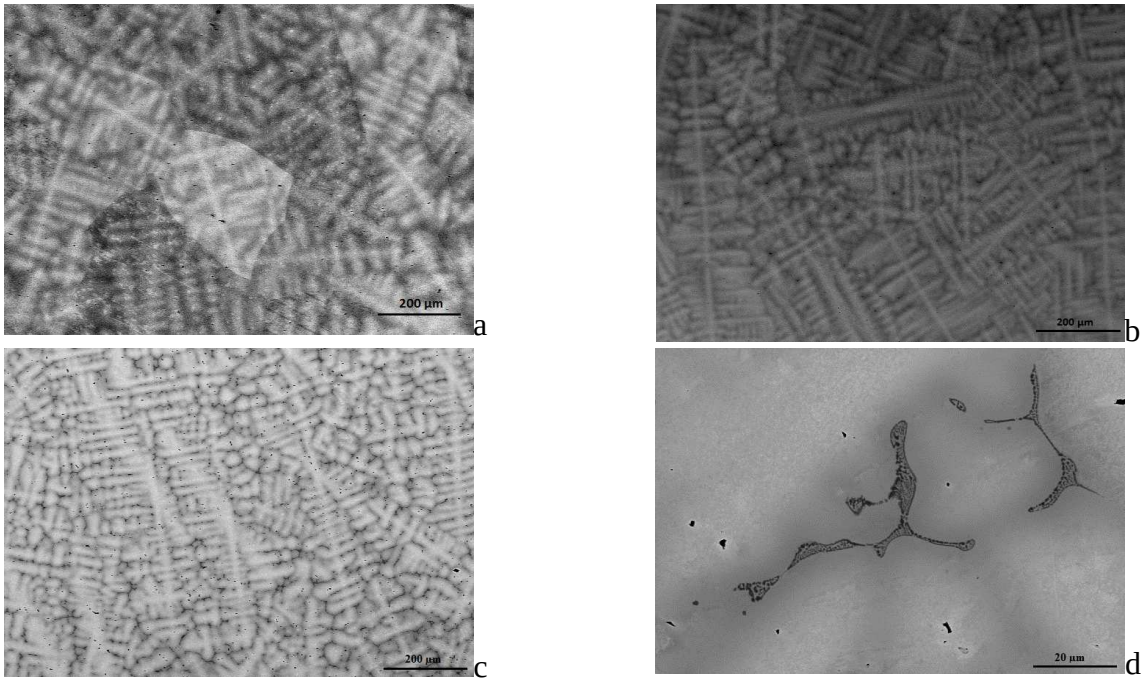
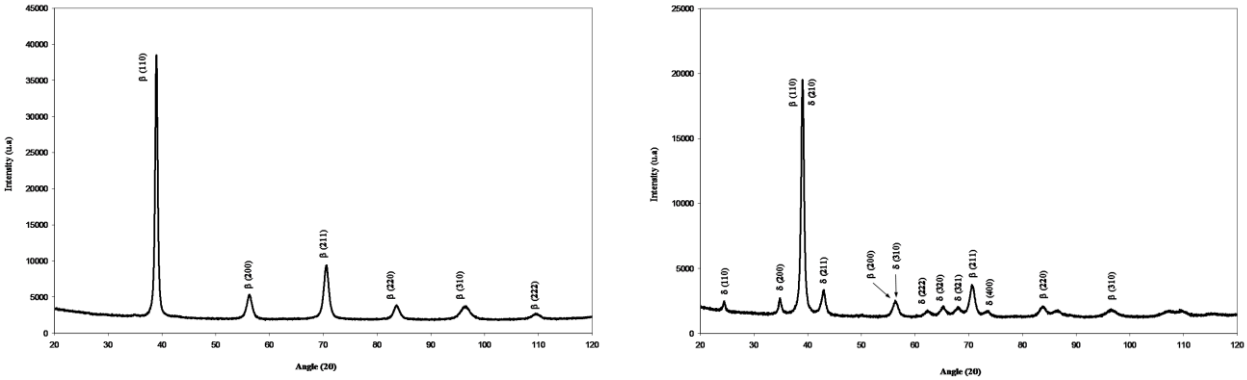


Fig. 1. Representative microstructures with BSE imaging of as-cast conditions, (a) of the M1 alloy, (b) of the M2 alloy with 1 at.% of Si, showing none presence of silicide, (c) and (d) of the M3 alloy showing a precipitation of silicide mainly located at interdendritic spaces.

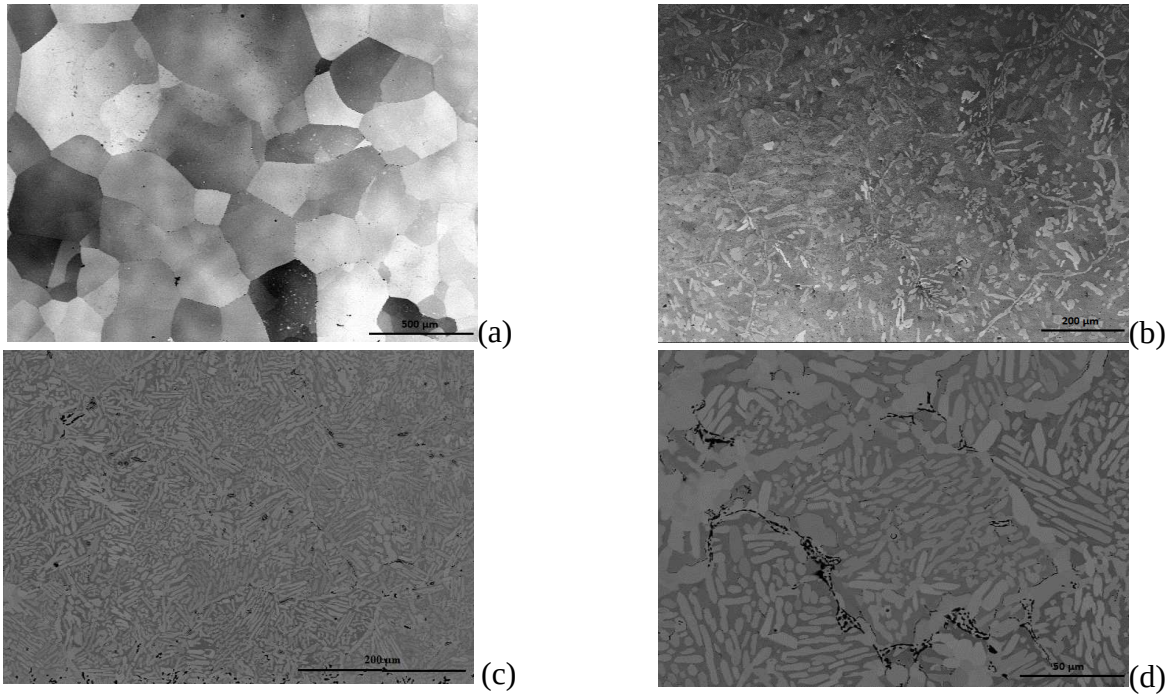


(a) (b)

Fig. 2. (a) XRD pattern of the solid solution phase of the M1 alloy in as-cast condition (b) XRD pattern of M3 alloy treated at 1200°C/50h.

1200°C/50h/furnace cooling

Following the heat treatment at 1200°C/50h, the M3 alloy displays an extensive precipitation of a second phase (Fig. 3c) was identified through XRD to be the δ-phase (Nb_3Al) (Fig.2b). These observations were confirmed by EDS analysis showing a chemical composition type $(Nb, Ti)_3(Al, Si)$ (Table 2). Furthermore, the presence of black precipitates located at grain boundary was revealed by BSE image (Fig. 3d) and identified to be the $(Ti,Nb)_5(Si, Al)_3$ type silicide. The δ-phase has been also detected in alloy M2 (Fig. 3b) but to a lesser extent than in alloy M3 and none silicide was observed. The M1 alloy (0 at.% Si), exhibits an equiaxed grains microstructure, the dendritic solidification microstructure has been erased after the treatment of 1200°C/50h (Fig. 3a).



(a) (b) (c) (d)

Fig. 3 (a) Backscattered SEM Micrograph of cast + 1200°C/50h heat-treated M1 (0at.% Si) alloy showing equiaxed grains microstructure. (b) Backscattered SEM Micrograph of cast + 1200°C/50h heat-treated M2(1 at.% Si) alloy showing the presence of the δ-phase. (c) & (d) Backscattered SEM Micrographs of cast + 1200°C/50h heat-treated M3 (2 at.% Si) alloy showing an extensive precipitation of the δ-phase and the presence of silicides at grains boundaries and in previous interdentritic regions.

1400°C/24h/furnace cooling

The heat treatment of 1400°C/24h leads to a significant growth of the grain size in M1 alloy (without silicon addition). As seen in Fig. 4a, the average grains size of the M1 alloy is higher than the millimetre. Whereas in M3 alloy heat-treated at the same temperature, it seems that the grain growth has been limited because of the δ-phase and silicide precipitates at grains boundaries (Fig. 4c). EDS analysis shows the presence of $(Nb,Ti)_3(Al, Si)$ at grain boundaries (Fig. 4d and Table 2). Precipitation of silicide inside the grains is also observed (Fig. 4b). On the contrary to the treatment of 1200°C/50h, the M2 alloy exhibits a precipitation of silicide at grain boundaries and none δ-phase is observed after the treatment of 1400°C/24h (Fig. 4c).

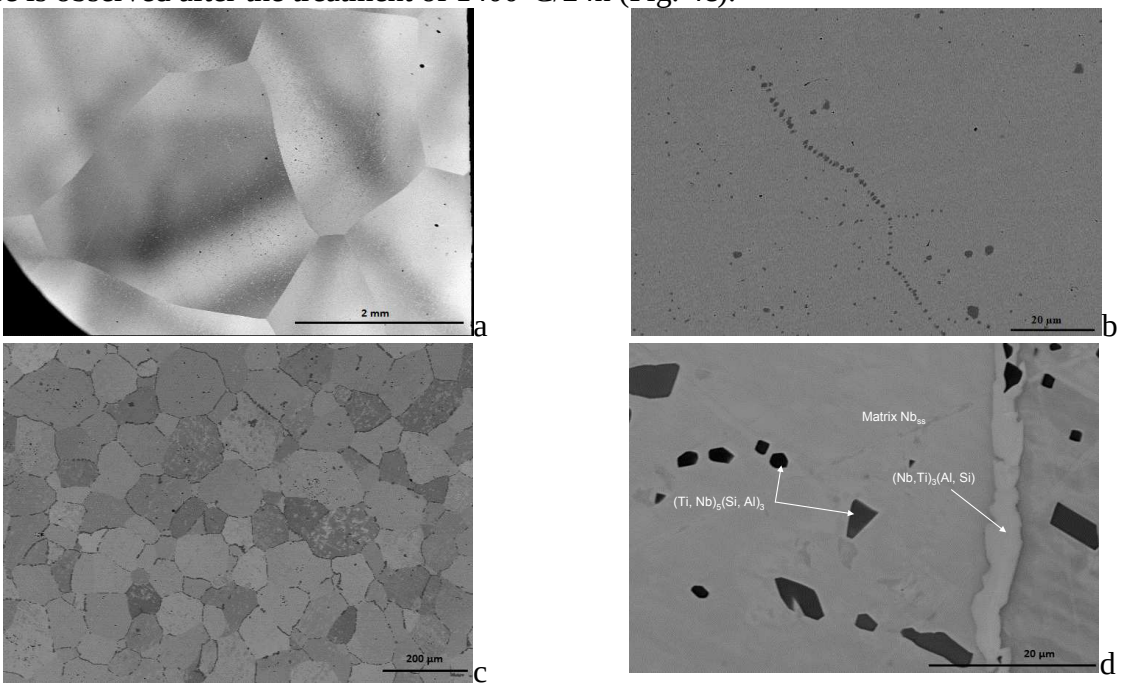


Fig. 4 (a) Backscattered SEM Micrograph of cast + 1400°C/24h heat-treated M1 (0at.% Si) alloy showing equiaxed grains microstructure. (b) Backscattered SEM Micrographs of cast + 1400°C/24h heat-treated M2 alloy showing the presence of δ-phase and silicide. (c) and (d) Backscattered SEM Micrographs cast + 1400°C/24h heat treated M3 alloy showing precipitation of silicide and δ- phase at grain boundaries.

Alloy Composition (at.%)	Heat Treatment	Phases	Phases Composition (at.%) Nb	Ti	Al	Si
51 Nb-34Ti-15Al	1400°C/24h	Nb_{ss}	49	34.8	16.2	-
	1200°C/50h	Nb_{ss}	48.8	33.5	17.7	-
50.4Nb-33.6Ti-15Al-1Si	1400°C/24h	Nb_{ss}	48.3	39.7	10.2	1.8
		$(Ti, Nb)_5(Si, Al)_3$	32.6	34.4	6.6	26.4
	1200°C/50h	Nb_{ss}	49.8	36.9	12.3	1.0
		$(Nb, Ti)_3(Al, Si)$	54.2	26.4	16.4	3
49.8Nb-33.2Ti-15Al-2Si	1400°C/24h	Nb_{ss} (β)	44.6	37.9	15.9	1.6
		$(Nb,Ti)_3(Al, Si)$	47.7	29.8	19.2	3.3
		$(Ti, Nb)_5(Si, Al)_3$	27.8	33.5	7.3	31.4
	1200°C/50h	Nb_{ss} (β)	41.7	44.5	12.3	1.5
		$(Nb,Ti)_3(Al, Si)$	44.4	32	19.3	4.3
		$(Ti, Nb)_5(Si, Al)_3$	26.3	39.8	9.2	24.7

Table 2 Alloy compositions and phase analysis (the accuracy of the EDX measurements is about ±10%).

For the Nb-34Ti-15Al alloy, the silicon solubility in the Nb solid solution, during the solidification seems to be between 1 at.% and 2 at.%. Indeed, primary precipitates of silicide were observed at as-cast condition for the alloy with 2 at.% of silicon, whereas in the case of M2 alloy (1 at.% of Si), silicide precipitated only after the treatment of 1400°C/24h.

Silicon addition seems to promote the precipitation of the δ-phase instead of the precipitation of silicide in Nb-34Ti-15Al alloy, especially for the temperature of 1200°C. Thus, one of the silicon

addition effects is to increase the β transus of the ternary system NbTiAl, which was estimated by [6] at 1125°C, and presently is to be higher than 1200°C with just 1 at.% of Si.

For higher heat treatment (1400°C/24h), silicides were observed in both M2 and M3 alloys, whereas the δ-phase was observed only in M3 alloy and in much lesser extent than at 1200°C. According to previous observations, an addition of 2at.% Si induces a β-transus higher than 1400°C. The microstructure the alloy at this temperature consists in a mixture of β (Nb_{ss}), δ-phase and silicide.

3.2. Compression tests

The compression stress-strain curves for the three alloys in as-cast condition are shown in Fig. 5. From theses σ-ε curves, the 0.2% strain compressive yield strength has been determined. For both testing temperatures, room temperature and 800°C, it was observed a significant increase of the yield strength with silicon content (Fig. 5). The yield strength was raised by 165 MPa by increasing the silicon content to 1at.%, and raised by 340 MPa with 2at.% silicon addition. For the three tested alloys, the compression tests conducted at 800°C displayed a markedly decrease of yield strength compared to those carried out at room temperature (Fig. 5-6). However, the yield strength of the M1 alloy, without silicon addition, was mostly affected by the higher testing temperature than the M3 alloy containing 2 at.% silicon, which exhibited a decrease of the yield strength to a lesser extend (Fig. 6). The compression stress-strain curve of the M2 alloy tested at 800°C shows a slight yield drop (Fig. 5).

Thus, the Fig. 6 clearly shows that, an addition of silicon, even in relatively low amounts, has a significant beneficial effect on the yield strength. Especially, its addition seems to improve the high temperature properties of the alloys.

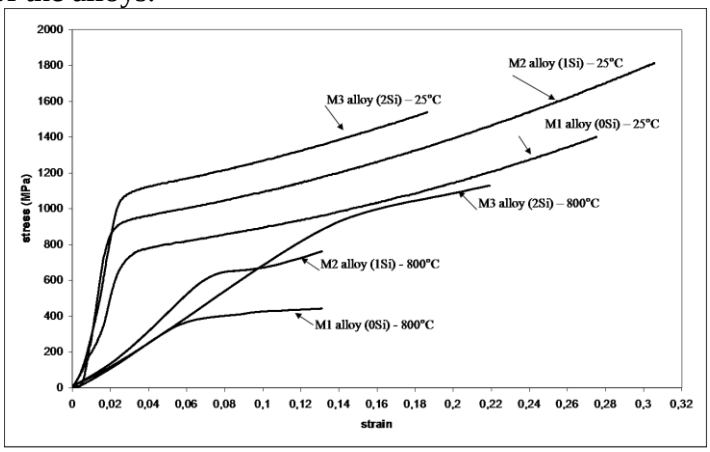


Fig. 5 Compression stress-strain curves for the three alloys at as-cast condition. The testing temperatures were room-temperature and 800°C The strain rate was 10^{-4} s^{-1}.

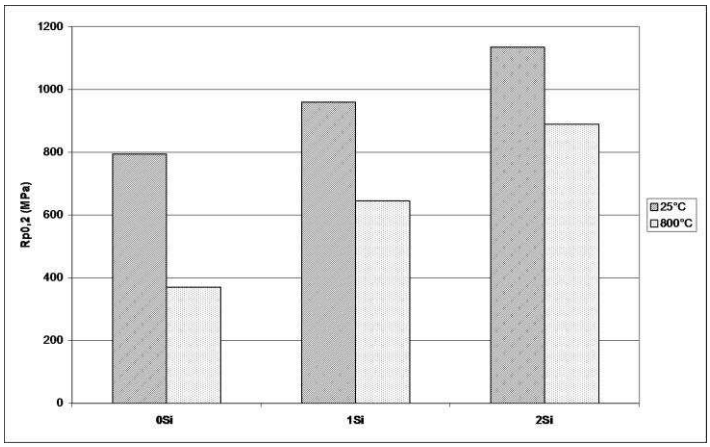


Fig. 6 Compression yield strength versus silicon content for the three alloys tested at room-temperature and at 800°C.

4. Summary and conclusion

In the present paper, Nb-base refractory alloys based on Nb-35Ti-15Al (at.%) and doped with small amount of Si (1 and 2 at%) have been studied. The silicon addition effects on the microstructure features and mechanical properties (compression test) have been investigated.

Si addition promotes extensive precipitation of the δ-(Nb, Ti)3(Al, Si) phase instead of silicide formation, thereby increasing the β/δ-transus temperature. Although a β/δ-transus of 1125°C for the ternary composition is reported in the literature , the transus of the NbTiAl -Si quaternary system is higher than 1200°C for 1at.% Si and higher than 1400°C for 2at.% Si.

Solubility of Si in Nbss appears to be low : although silicon content in Nbss after solidification is between 1 and 2 at%, secondary silicide precipitation is observed at 1400°C even for 1at% of silicon. The promotion of the δ phase by Si addition at 1200°C is also indicative of a low solubility in the Nb matrix, even at lower temperatures.

Compression tests were perfomed on as-cast condition, at both room temperature and 800°C. For this condition, Nbss matrix seems to be sursaturated in Si. It should be noted that verification has been made that no modification of the microstructure took place during high temperature testing. According to the results, the silicon addition has a significant beneficial effect on the yield strength for both temperatures and this effect increases with silicon content. Mechanical characterization of other heat treatment conditions should give indication of the effect of δ phase and secondary silicides on mechanical behaviour and therefore ways to optimise this alloy system.

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