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On the T_2-phase formation in mechanically alloyed Nb–Si and Nb–Si–B powders

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Abstract

The present work reports on the T_2-phase formation in mechanically alloyed Nb–37.5Si, Nb–25Si–12.5B, Nb–12.5Si–25B powders. Results indicated that Si and B atoms were dissolved into the Nb lattice to form supersaturated solid solutions during ball milling. The T_2-phase was formed in Nb–37.5Si powders after milling for 30 h. A large amount of T_2-phase was formed in Nb–25Si–12.5B and Nb–12.5Si–25B powders after heat treatment at 1600 °C for 1 h. The following lattice parameters of the T_2-phase were measured in Nb–37.5Si powders: $a = 6.5625$ nm and $c = 11.9017$ nm. In Nb–12.5Si–25B powders, it was noted a reduction of a and c values to 6.2317 and 11.6159 nm, respectively.

Keywords: Intermetallics; Mechanical alloying; X-ray diffraction

1. Introduction

Refractory materials such as RM-Si–B alloys (RM, refractory metal) have been potentially attractive for high-temperature structural applications due to their physical, chemical, mechanical properties such as high melting point, oxidation resistance, and mechanical properties [1–3]. In Nb–Si and Nb–Si–B systems, the Nb-richer alloys present microstructures containing a pseudo-ternary phase (known as T_2) with stoichiometry varying from α-Nb_5Si_3 (low temperature) to Nb_5SiB_2, depending on composition alloy [4,5].

Various studies involving the preparation of intermetallic compounds are reported, which were prepared from different routes such as arc-melting and powder metallurgy processes [6,7]. Non-equilibrium powder processing routes have been potentially desired to improve the mechanical properties from homogeneous and refined microstructures. Metastable and nanocrystalline materials can be produced by mechanical alloying process from elemental or pre-alloyed powder mixtures [8–11]. Amorphous phases and nanostructured powders can be formed during the milling process of Ti–Si and Nb–Si powder mixtures [12,13].

Studies on the preparation of Nb–Si binary alloys by mechanical alloying have been realized [14]. Recently, the mechanical alloying and further heat treatment of Nb–25Si–12.5B powders successfully produced a large amount of T_2-phase [15]. The present work reports the effect of boron-added ($x = 25$ at.%) in $Nb_{62.5}$–$Si_{(37.5-x)}$ powders during the mechanical alloying and the lattice parameters of T_2-phase.

2. Experimental procedure

The following high-purity elemental powders were used for preparation of Nb–37.5Si, Nb–25Si–12.5B, and Nb–12.5Si–25B alloys by mechanical alloying: Nb (min 99.0 wt.%, angular, <200 mesh) Si (99.999 wt.%, irregular, <200 mesh), and B (99.5 wt.%, angular, <200 mesh).

The milling process was carried out in a planetary Fritsch P-5 ball mill under argon atmosphere using stainless steel balls (19 mm diameter) and vials (225 mL), rotary speed of 200 rpm, and a ball-to-powder weight ratio of 10:1. To minimize an intense agglomeration of ductile starting powders the reverse operation was adopted. The starting and milled powders were handled into the Ar-filled glove box to minimize the atmospheric contamination and spontaneous ignition. Powder samples were collected into the vial after different milling times (1, 10, 30, 60, and 100 h).

Following, the Nb–Si–B milled powders for 100 h were uniaxially compacted (10 mm diameter) using 5 tonnes. To obtain the equilibrium microstructures the milled powders were heat-treated under argon atmosphere at 1600 °C for 1 h. Lower temperature and shorter times were used in this work to minimize the elemental and preferential evaporation during heating, comparing to those conditions previously adopted of 1700 °C for 4 h [15].

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The milled and heat-treated powders were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and microanalyses via energy dispersive spectrometry (EDS). XRD experiments were performed at room temperature using Ni-filtered Cu Kα radiation. The computer program Powdercell [16] was used to index the phases present in mechanically alloyed and heat-treated Nb–Si–B powders, and the phases present were indexed according to the JCPDS database files [17]. The lattice parameters of phases were measured by Rietvelt method [18]. SEM images of mechanically alloyed Nb–37.5Si, Nb–25Si–12.5B and Nb–12.5Si–25B powders were obtained in back-scattered electron mode. The Nb and Si contents of phases in heat-treated Nb–Si–B powders (1600 °C for 1 h) were measured by EDS analysis.

3. Results and discussion

Fig. 1 shows the XRD patterns of Nb–37.5Si and Nb–12.5Si–25B powders at different milling times. Initially, it was observed the presence of Nb and Si peaks only. A similar behavior was noted in binary and ternary powder mixtures during the initial milling stage, i.e., the broadening and reduced intensity of Nb and Si peaks in binary and ternary powder mixtures have occurred. The Si peaks disappear after milling for 10 h, suggesting that metastable phases are being formed. At moment, the Nb peaks were slightly moved toward in the direction of higher diffraction angles, indicating that the Si and/or B atoms were dissolved into the Nb lattice to form supersaturated solid solutions, as are shown in Fig. 1. In addition, it can be observed that the intensity of Nb peaks was reduced with the increasing of boron amount in powder mixtures, suggesting that the mechanical alloying could be attained in shorter milling times. A halo was formed in Nb–37.5Si, Nb–25Si–12.5B, and Nb–12.5Si–25B powders after milling for 30 h, which can be associated to the formation of an amorphous phase. Previous work has indicated that an amorphous phase can be formed during ball milling in Nb–Si powder mixtures [14]. In Nb–37.5Si powders, the T_2-phase was partially formed after milling for

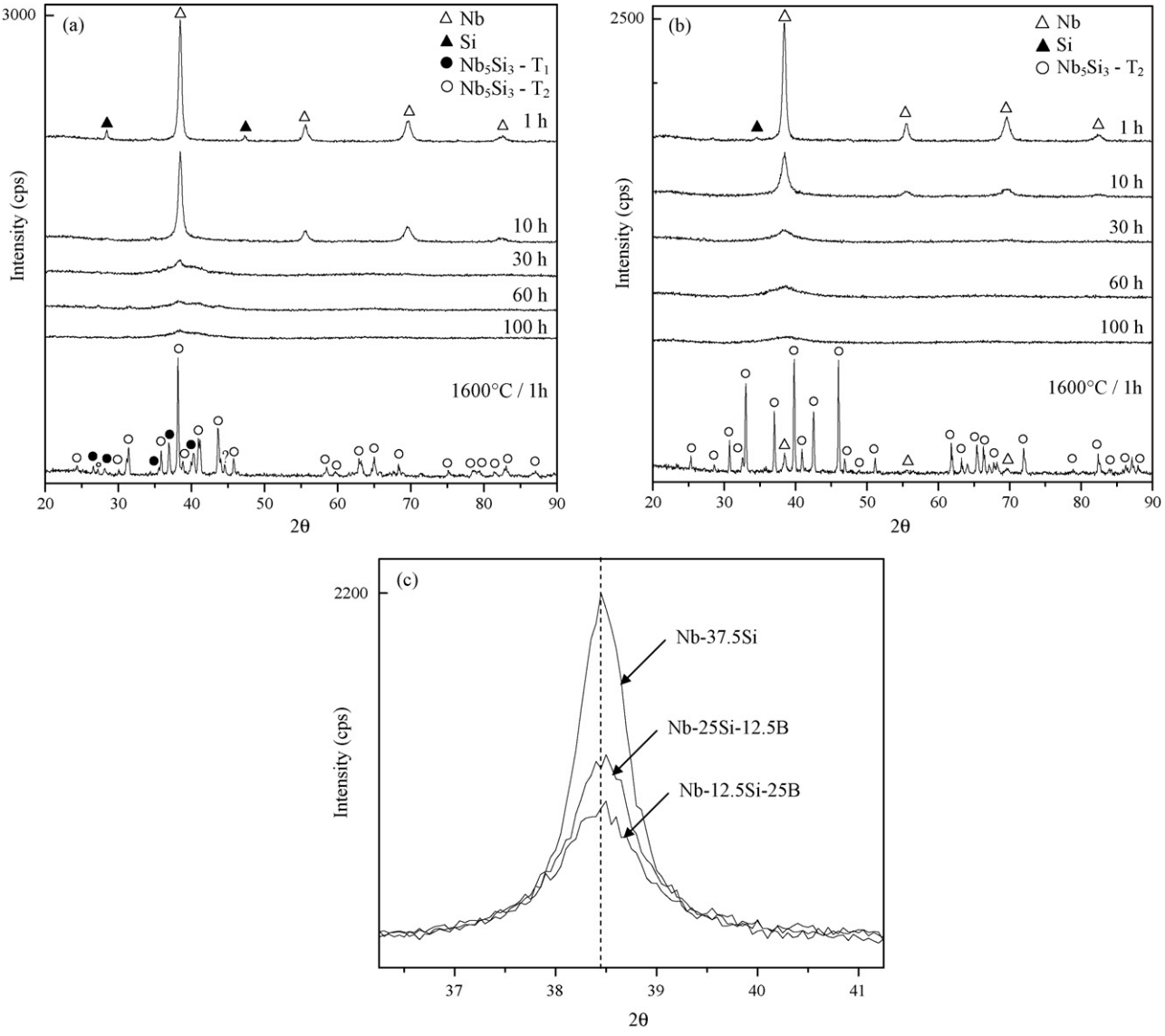

Fig. 1. XRD patterns of: (a) Nb–37.5Si and (b) Nb–12.5Si–25B powders at different milling times, and after heat treatments at 1600 °C for 1 h. In (c), the variation of lattice parameters in Nb–Si and Nb–Si–B powders after milling for 10 h.

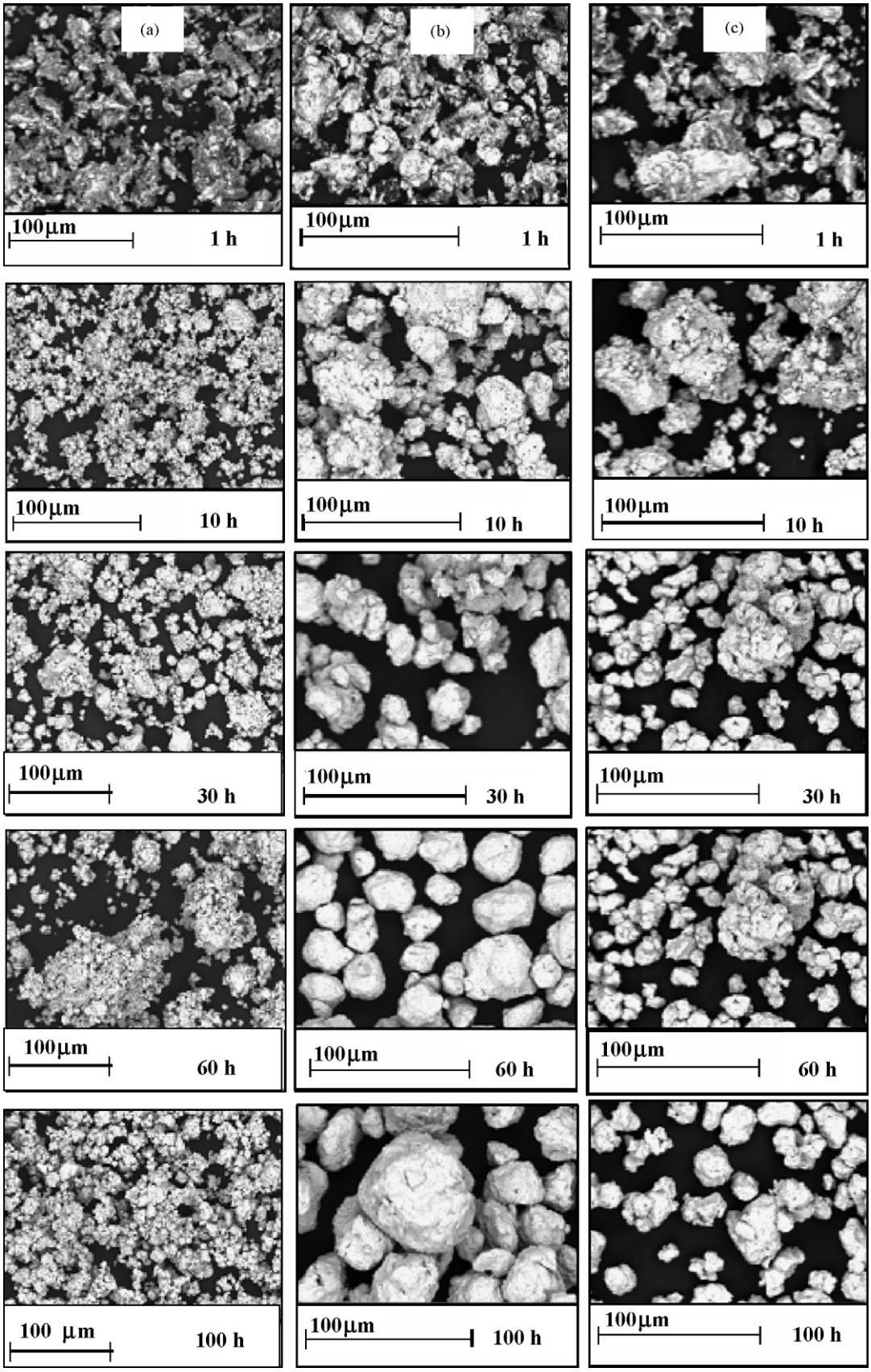

Fig. 2. SEM images of: Nb–37.5Si; (b) Nb–25Si–12.5B; (c) Nb–12.5Si–25B powders at different milling times.

60 h. In contrary, no intermetallic peaks were identified in Nb–25Si–12.5B and Nb–12.5Si–25B powders after milling for 100 h.

The morphologies of Nb–37.5Si, Nb–25Si–12.5B, and Nb–12.5Si–25B powders at different milling times are shown in Fig. 2. Initially, the Nb (and B) and Si powders presented angular and irregular morphologies, respectively. Brittle Si and B particles are fragmented in earlier milling stage, which were incrusted in softer Nb matrix. The sizes of powder particles were reduced in Nb–37.5Si powder mixture after milling for 10 h, while the larger powder particles can be found in Nb–25Si–12.5B and Nb–12.5Si–25B powders owing the reduced amount of brittle components in starting powder mixtures with the boron amount increased up to 25 at.%. In this sense, the cold-welding mechanisms more intense were observed in Nb–25Si–12.5B and Nb–12.5Si–25B powders. In both the cases, it was observed the presence of powder particles with rounded morphologies after milling for 30 h. Moreover, the presence of clusters was noted in finer Nb–37.5Si powder particles. Following, the sizes of powder particles were again increased until milling for 100 h. The clusters previously formed in Nb–37.5Si powders were broken after milling for 100 h probably owing the formation of an intermetallic phase (T_2-phase).

The XRD patterns of mechanically alloyed Nb–37.5Si, Nb–25Si–12.5B, and Nb–12.5Si–25B powders after heat treatment at 1600 °C for 1 h are shown in Fig. 1. Results have indicated that a large amount of T_2-phase was formed in these heat-treated alloys. Accordingly to the previous work [15], its lattice parameters were varied from Nb–37.5Si and Nb–12.5Si–25B compositions. The following lattice parameters of the T_2-phase were measured in Nb–37.5Si powders: $a = 6.5625$ nm and $c = 11.9017$ nm. In Nb–12.5Si–25B powders, the a and c values were reduced to 6.2317 and 11.6159 nm, respectively.

SEM images of heat-treated Nb–37.5Si, Nb–25Si–12.5B and Nb–12.5Si–25B alloys are shown in Fig. 3. The microstructures

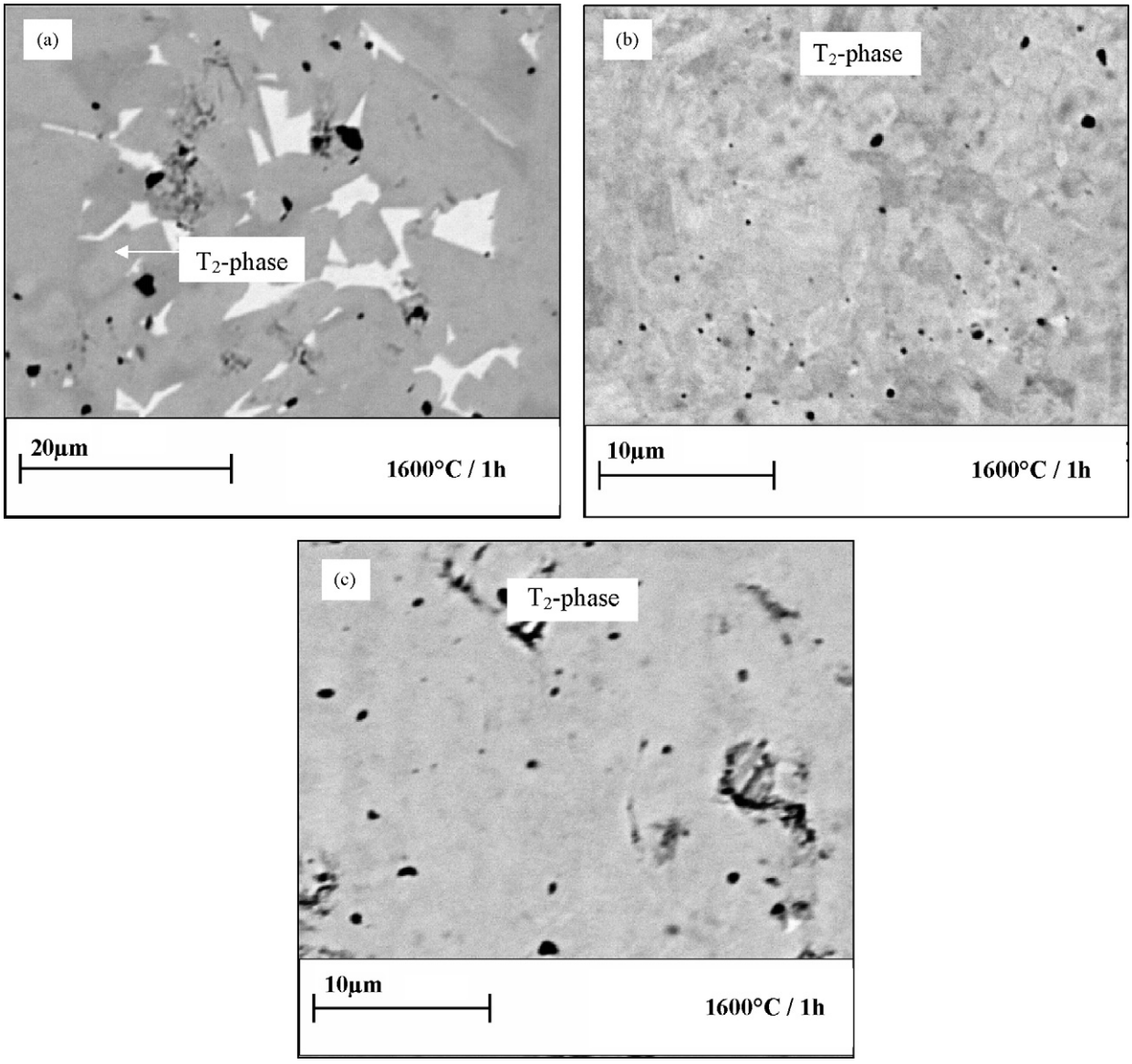

Fig. 3. Micrographs (SEM) of the: (a) Nb–37.5Si; (b) Nb–25Si–12.5B; (c) Nb–12.5Si–25B alloys after heat treatment at 1600 °C for 1 h.

were formed with a majority of T_2-phase as matrix. A small amount of other Nb_{ss} (ss, solid solution) was also observed in these alloys after heat treatment at 1600 °C for 1 h, indicating that a preferential evaporation during heating and/or the heterogeneity reached during ball milling because the intense cold-welding mechanism could have occurred. The T_2-phase formed in mechanically alloyed Nb–37.5Si, Nb–25Si–12.5B, and Nb–12.5Si–25B powders after heat treatments presented the Si contents varying between 32.1 and 36.6, 20.2 and 24.1, and 11.6 and 13.4 at.%, respectively.

4. Conclusions

The T_2-phase was obtained in the Nb–37.5Si, Nb–25Si–12.5B and Nb–12.5Si–25B alloys produced by mechanical alloying followed by a heat treatment of 1 h at 1600 °C.

Finer powder particles were found in Nb–37.5Si powders during ball milling owing the larger amount of brittle components in starting powder mixture.

The T_2-phase presented the following lattice parameters in mechanically alloyed Nb–37.5Si powders: $a = 6.5625$ nm and $c = 11.9017$ nm. It was noted a reduction of these values in mechanically alloyed Nb–12.5Si–25B powders, $a = 6.2317$ and $c = 11.6159$ nm. EDS analyses confirmed that the Si contents of the T_2-phase were reduced with the added boron amount.

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