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Preparation of Nb–25Si, Nb–37.5Si, Nb–66.6Si powders by high-energy ball milling and subsequent heat treatment

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Abstract

The present paper reports on the syntheses of the Nb_3Si, α-Nb_5Si_3 and $NbSi_2$ compounds by mechanical alloying and subsequent heat treatment. The milling process was carried out in a planetary Fritsch P-5 ball mill under argon atmosphere using stainless steel balls and vials, rotary speed of 200 rpm and a ball-to-powder weight ratio of 10:1. Following, the milled powders were heat-treated at 1600 °C for 1 h in order to obtain the equilibrium microstructures. The milled and heat-treated powders were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), microanalysis via energy dispersive spectrometry (EDS). Results indicated that the silicon atoms were dissolved into the Nb lattice during milling to form supersaturated solid solutions. The Nb_3Si compound was formed after heat treatment at 1600 °C for 1 h only, while the Nb_5Si_3 and $NbSi_2$ compounds were successfully formed during ball milling. Results have indicated that a significant iron contamination close to 5 at% was found in mechanically alloyed Nb–25Si, Nb–37.5Si and Nb–66Si powders. Consequently, the nominal compositions of Nb–Si powders were altered and other phases were also formed after heat treatment at 1600 °C for 1 h.

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1. Introduction

Nb-based alloys have been considered for high-temperature structural and microelectronic applications due to their physical and chemical properties, such as high melting point and oxidation resistance [1–5].

The following stable solid phases are reported in the accessed Nb–Si phase diagram: Nb_{SS} (ss-solid solution), Nb_3Si, α-Nb_5Si_3 (low temperature), β-Nb_5Si_3 (high temperature), $NbSi_2$ and Si_{SS}. The Nb_3Si phase is formed from the melt by the peritectic reaction $L + Nb_5Si_3 \Leftrightarrow Nb_3Si$, while the Nb_5Si_3 and $NbSi_2$ phases are formed by congruent transformations [6]. Eutectic microstructure formed by the Nb_{SS} and Nb_3Si phases can be produced in as-cast alloys containing higher Nb amount.

Non-equilibrium powder processing techniques are employed to produce nanocrystalline materials and metastable structures, which can be successfully obtained depending on the starting powders, type of mill and milling parameters. Various intermetallic compounds have been prepared by different high-energy ball milling processes [7–10]. Previous works reported on the phase transformations in Nb–16 at% Si powders (eutectic composition) during ball milling using a shaker mill, and the in situ explosive $NbSi_2$ formation in Nb–66 at% Si powders occurred during high-energy ball milling [11,12]. The present work reports on the synthesis by mechanical alloying of Nb_3Si, α-Nb_5Si_3 and $NbSi_2$ compounds.

2. Experimental procedure

The Nb–25Si, Nb–37.5Si and Nb–66Si elemental powder mixtures (at%) were used to produce by mechanical alloying the Nb_3Si, α-Nb_5Si_3, $NbSi_2$ compounds, respectively. The following high-purity starting powders were used in this work: Nb (min 99.0 wt%, angular, <200 mesh) and Si (99.999 wt%, irregular, <200 mesh).

The milling process was carried out in a planetary Fritsch P-5 under argon atmosphere using rotary speed of 200 rpm, stainless steel balls (19 mm diameter)

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and vials (225 ml), and a ball-to-powder weight ratio of 10:1. After different milling times (1, 10, 30, 60 and 100 h) the milling process was interrupted and small amounts of the milled materials were taken out for analysis. To minimize the atmospheric contamination and a spontaneous ignition Ar-filled glove box was used to manipulate the reactive powders. Following, the milled powders were heat-treated at 1600 °C for 1 h under argon atmosphere in order to obtain equilibrium microstructures.

The milled and heat-treated powders were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and microanalysis via energy dispersive spectrometry (EDS). XRD experiments were performed at room temperature in a Seifert equipment using Ni-filtered Cu Kα radiation. The computer program Powdercell [13] was used to index the phases present in milled and heat-treated Nb–Si powders, and the phases present were indexed according to the JCPDS database files [14]. SEM images were obtained in the backscattered electron mode, and the Nb and Si contents of the phases formed in heat-treated Nb–Si alloys were measured by microanalysis via EDS. The iron amount picked up in mechanically alloyed Nb–Si powders was also determined.

3. Results and discussion

XRD patterns of Nb–25Si, Nb–37.5Si and Nb–66Si powders at different milling times are shown in Fig. 1. Initially, it was noted a similar ball milling behavior between the Nb–25Si, Nb–37.5Si and Nb–66Si powders, i.e., the silicon atoms were dissolved into the Nb lattice to form supersaturated solid solutions after milling for 10 h. At this moment, it occurred the broadening and the reduction on the intensity of Nb peaks, and the Si peaks disappeared in Nb–25Si and Nb–37.5Si powders

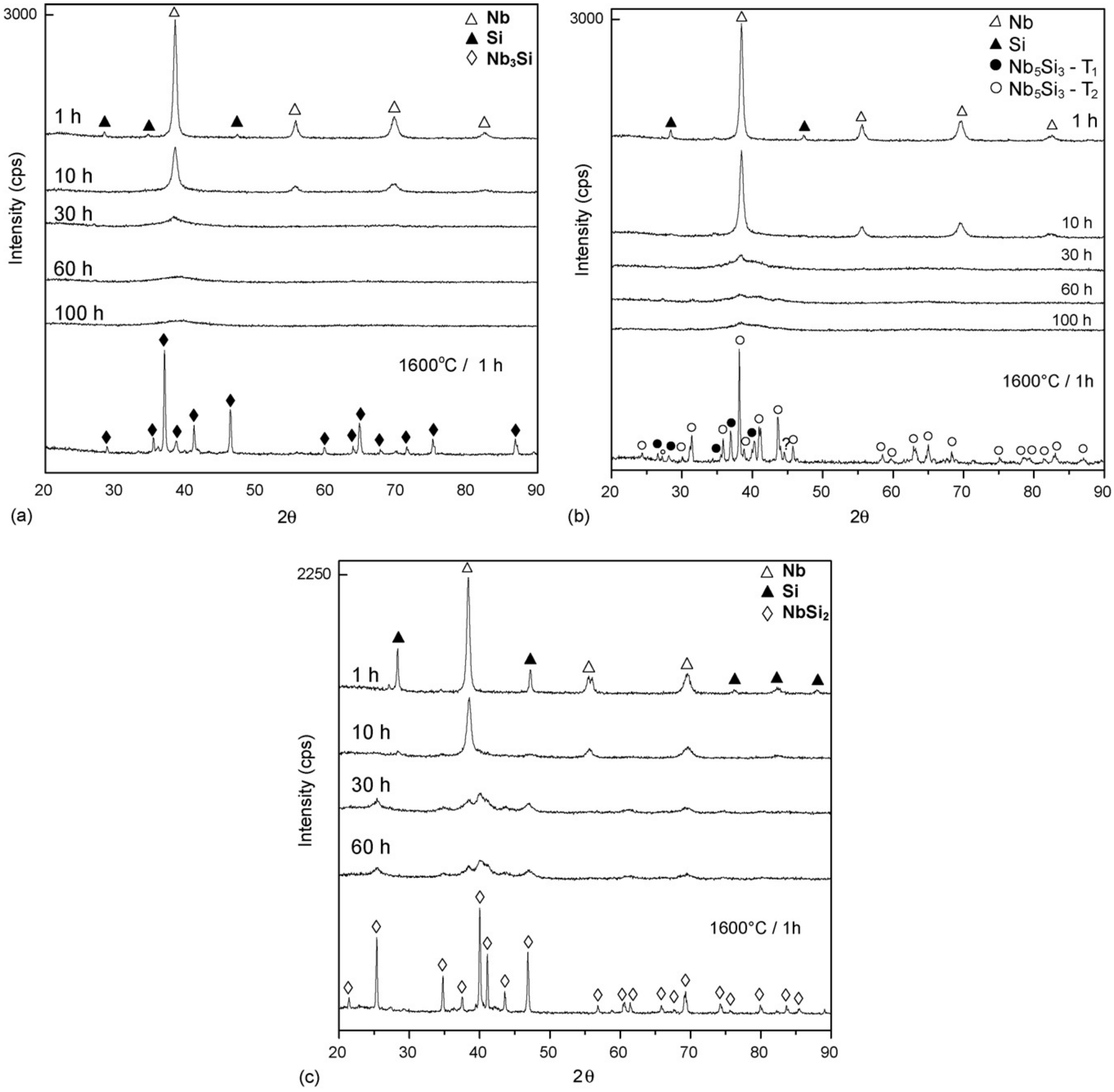

Fig. 1. XRD patterns of (a) Nb–25Si, (b) Nb–37.5Si and (c) Nb–66Si powders at different milling times and after heat treatment at 1600 °C for 1 h.

milled for 10 h. In addition, it was also noted that the Nb peaks were slightly moved toward the direction of higher diffraction angles, suggesting that metastable structures were formed. In Nb–66Si powders milled for 10 h, it was noticed the presence of Si peaks, indicating that its non-equilibrium solid solubility was reached. The reduction on the intensity of Nb peaks was more pronounced in powder mixtures containing higher silicon amount. Following the ball milling, XRD results suggested that

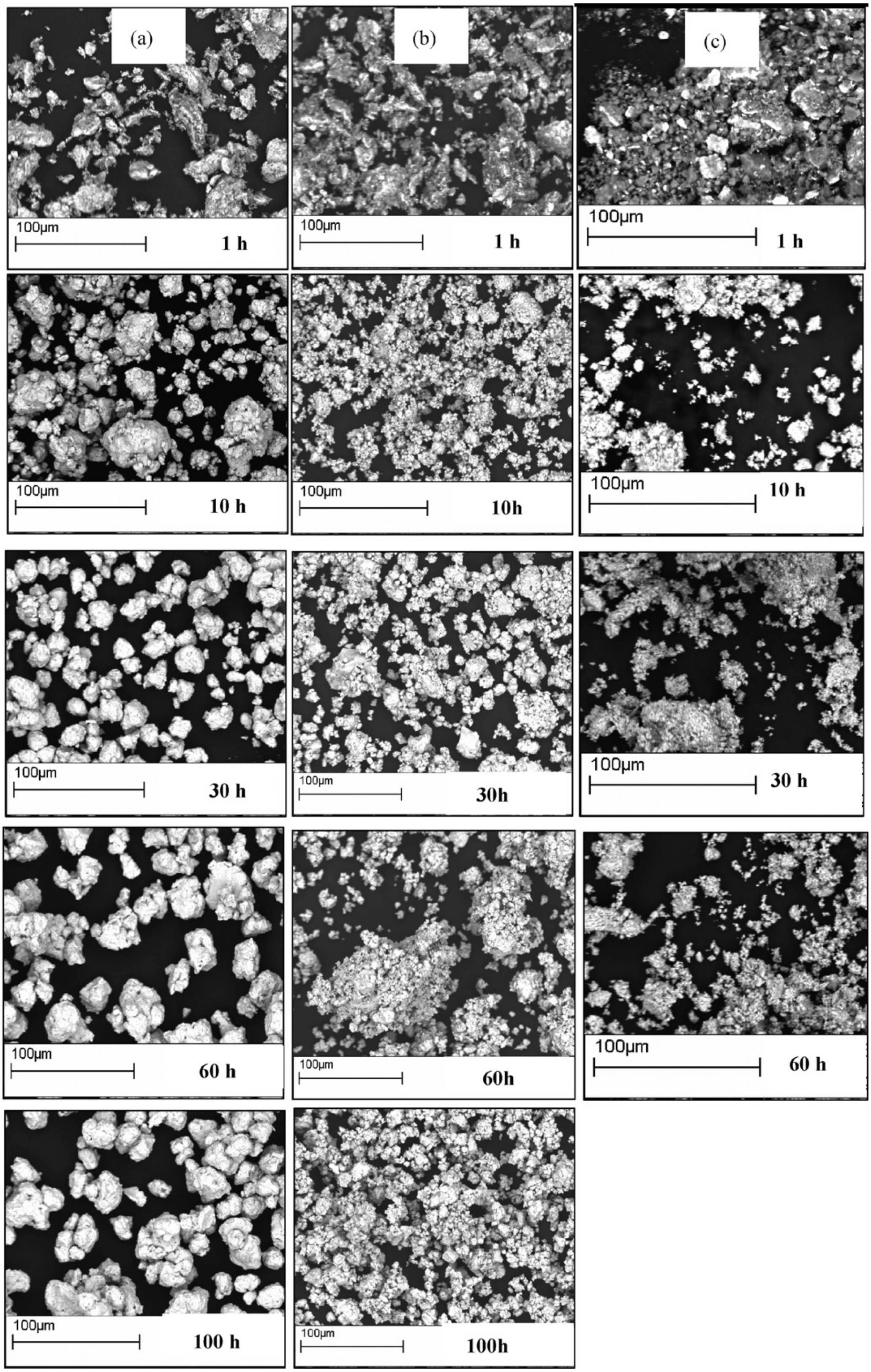

Fig. 2. SEM images of (a) Nb–25Si, (b) Nb–37.5Si and (c) Nb–66Si powders at different milling times.

an amorphous phase was formed in Nb–25Si powders milled for 100 h. Previous works have reported that amorphous structures can be formed in Nb–Si powders during the mechanical alloying [15]. In Nb–37.5Si and Nb–66Si powders, the Nb_5Si_3 and $NbSi_2$ phases were formed after milling for 60 and 30 h, respectively. However, the lower intensity values of characteristic peaks have suggested that the atomic disordering of these intermetallic compounds was reached in Nb–37.5Si and Nb–66Si powders milled for 100 and 60 h, respectively.

Fig. 2 shows the morphology of Nb–25Si, Nb–37.5Si and Nb–66Si powders at different milling times. Initially, it was noted an inhomogeneous distribution and irregular morphology of starting powder particles. Large and rounded particles were found in Nb–25Si powders milled for 10 h due to an intense cold-welding mechanism occurred during ball milling with powder mixtures containing a large amount of ductile component. In Nb–25Si powders milled for 30 h, the particle sizes were reduced probably owing the severe plastic deformation and/or formation of an intermetallic phase. However, the cold-welding mechanisms were more pronounced in Nb–25Si powders milled for 100 h, and their particle sizes were then increased. Finer powder particles with rounded morphology and a homogeneous distribution were observed in mechanically alloyed Nb–37.5Si (60 h) and Nb–66Si (30 h) powders, indicating that the α-Nb_5Si_3 and $NbSi_2$ phases were formed during ball milling. Finer powder particles and clusters were found in Nb–37.5Si and Nb–66Si powders milled for 100 and 60 h, respectively.

XRD patterns of mechanically alloyed Nb–25Si, Nb–37.5Si and Nb–66Si powders after heat treatment at 1600 °C for 1 h are shown in Fig. 1. Results indicated the major presence of the Nb_3Si, α-Nb_5Si_3 and $NbSi_2$ phases in Nb–25Si, Nb–37.5Si and Nb–66Si, respectively. It was still noted that the peaks of the Nb_3Si phase were moved in the direction of lower diffraction angles in heat-treated Nb–25Si powders. Peaks of the β-Nb_5Si_3 (high temperature) phase were also indexed in XRD pattern of the heat-treated Nb–37.5Si alloy.

SEM images of the heat-treated Nb–25Si, Nb–37.5Si, Nb–66Si alloys are shown in Fig. 3. The microstructure of the heat-treated Nb–25Si alloy indicated the presence of the Nb_3Si phase as matrix, which dissolved close to 9.0 at% Fe (see

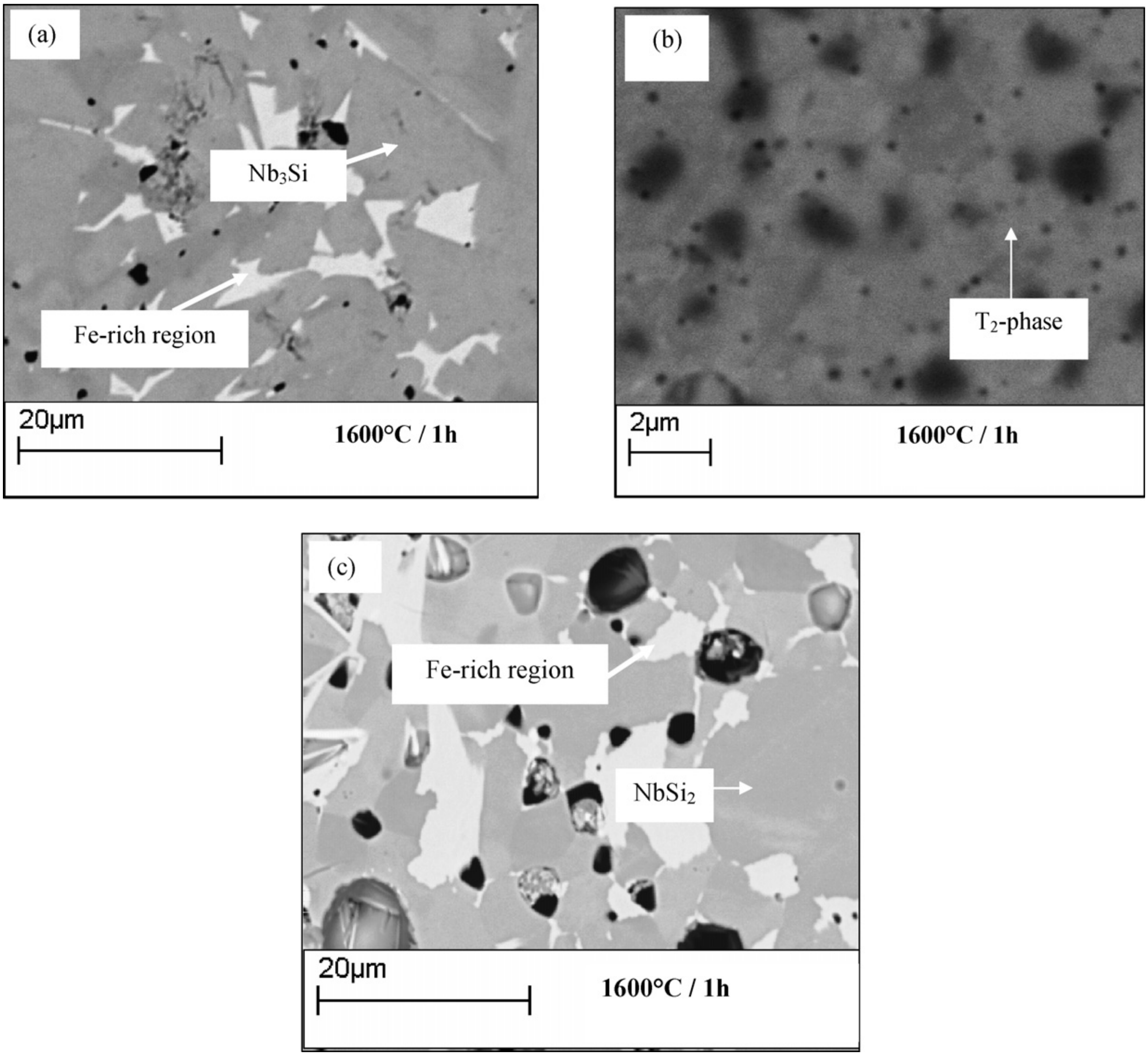

Fig. 3. Micrographs (SEM) of the (a) Nb–25Si, (b) Nb–37.5Si and (c) Nb–66Si alloys after heat treatment at 1600 °C for 1 h.

Fig. 3a). Thus, the displacement of Nb_3Si peaks in heat-treated Nb–25Si powders previously cited occurred preferentially due to an excessive iron contamination. In addition, it was also observed the presence of another phase with Nb, Fe and Si contents (at%) in the range 58.6–60.6, 20.1–26.2 and 13.3–15.6, respectively. The microstructure of the heat-treated Nb–37.5Si alloy indicated the presence of the α-Nb_5Si_3 phase as matrix, which it presented low iron solubility (see Fig. 3b). Moreover, it was also identified the presence of another phase containing Nb, Fe, Cr and Si contents close to 35.5, 35.5, 8.0 and 21.0 at%. In the heat-treated Nb–66Si alloy, the silicon contents of the $NbSi_2$ phase (matrix) were varied between 64.9 and 65.9 at%, and another unknown phase with Nb, Fe, Cr and Si contents close to 40.4, 16.5, 1.9 and 41.2 at% was also determined by EDS analyses. Results have indicated that a significant iron contamination lower than 5 at% was found in heat-treated Nb–25Si, Nb–37.5Si and Nb–66Si alloys. Consequently, the nominal compositions of starting powders were altered and other phases were also formed after heat treatments at 1600 °C for 1 h. The presence of SiO_2-based precipitates dissolving significant niobium and iron amounts was also detected in these heat-treated alloys.

4. Conclusions

The mechanical alloying and heat treatment successfully produced the Nb_3Si, Nb_5Si_3 and $NbSi_2$ compounds from Nb–25Si, Nb–37.5Si and Nb–66Si elemental powder mixtures, respectively.

Supersaturated solid solutions were formed in Nb–25Si, α-Nb–37.5Si and Nb–66Si powders after milling for 10 h. The α-Nb_5Si_3 and $NbSi_2$ phases were formed in Nb–37.5Si and Nb–66Si powders milled for 60 and 30 h, respectively. XRD results suggested that an amorphous phase was formed in Nb–25Si powders milled for 100 h, and no intermetallic peak was identified in powder mixtures containing smaller Si amount.

The Nb_3Si phase was successfully formed in Nb–25Si powders after heat treatment at 1600 °C for 1 h only, which presented iron contents close to 9.0 at%. Other phases containing high iron and chromium contents were also formed in heat-treated Nb–25Si, Nb–37.5Si and Nb–66Si alloys due to an excessive contamination from the milling medium.

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