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Structural evolution during mechanical alloying and annealing of a Nb-25at%Al alloy

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Mixtures of pure elemental Al and Nb powders of Nb-25at%Al composition was mechanically alloyed, and structural evolution during high energy ball milling has been examined. Al dissolved in Nb from the early stage of the ball milling, and amorphization became noticeable after longer than five hours of milling. However the dissolution of Al in Nb was not completed before the amorphization. No intermetallic phase formed during the mechanical alloying. Before complete amorphization, metastable nitride of $Nb_{4.62}N_{2.14}$ (i.e., β-NbN) with hexagonal structure has formed in nanocrystalline size through nitrogen incorporation from ambient environment. The lattice parameter of Nb increased significantly (up to 3.3433 Å after 5 hours of milling) during the milling. Upon annealing above 950 °C, Nb_2Al became the dominant feature with the β-NbN, and Nb_3Al did not form from the samples milled at ambient environment. Nb_3Al appeared only from a sample milled at Ar environment. Structural evolution during mechanical alloying of the Nb-Al system is critically dependent the upon milling environment. *© 2000 Kluwer Academic Publishers*

1. Introduction

In the Nb-Al binary system, three aluminides form by peritectic reactions. They are Nb_3Al, Nb_2Al and $NbAl_3$, and being investigated as potential structural materials for high temperature applications. Among the compounds in the Nb-Al system, Nb_3Al with A15 structure is considered to be the most promising candidate because of its high melting point, oxidation resistance, creep properties and low density. Single phase Nb_3Al is very brittle at low temperatures due to its complex crystal structure and limited slip system [1, 2]. Therefore, studies on the niobium aluminide are directed to increase toughness for possible structural applications. Small amount of deformable Nb_{ss} (Nb_{ss} means solid solution of Nb) prevents stress concentration at triple junctions, and thus formation of voids or microcracks is delayed [1, 3]. Another way to increase ductility in intermetallics is to synthesize fine-grain microstructure [2, 4]. Fine-grain microstructure promotes grain boundary sliding at elevated temperatures and thus enhances plasticity of a system where dislocation slip within grains is limited. The $Nb_3Al + Nb_{ss}$ material can be processed into fine grain sizes by thermo-mechanical processing currently utilized for superalloys. Fine-grained $Nb_3Al + Nb_{ss}$ alloy has been produced using hot isostatic press (HIP) consolidation of the mechanically alloyed (MA) powders, preliminary study exhibited high strain-rate sensitivity of 0.49 and demonstrated a possibility of enhancing ductility at elevated temperatures when powders were suitably prepared by the mechanical alloying step [5].

Intermetallic compounds with nanoscale microstructures can be produced by the mechanical alloying either through direct synthesis of elementals powders or transformation of amorphous phases obtained. Hellstern *et al.* reported an earlier work on MA of the Nb-Al system [4]. Recently, Peng *et al.* studied the effect of MA on nanostructure formation, amorphization and compound formation in the Nb-Al system, and reported that the sequence of phase formation varies widely depending upon Al-content [6]. When Al-content was less than 60 at %, the supersaturated Nb(Al) became amorphous state after long hours of milling, and annealing was needed to produce nanocrystalline forms of Nb_3Al and Nb_2Al. However, the $NbAl_3$ formed directly during the MA process in Al-rich compositions. The authors analyzed that 60 at % Al has dissolved in Nb during the solid-state reaction. However this value is unbearably higher than the solubility limit of Al in Nb at equilibrium state. The objective of this study is to identify structural evolution in the Nb-25at%Al composition during high energy ball milling in detail so that nanostructure synthesis of the niobium aluminides during P/M consolidation of the milled powders could be suitably understood.

2. Experimental

Elemental Nb and Al powders (99.9% purity, 325 mesh Nb and 200 mesh Al, respectively) were used as starting materials, and mixtures of Nb-25at%Al composition were high-energy ball milled in an ambient environment. A SPEX Mixer-Mill (Model 8000) with a 304 stainless steel vial (57 mm diameter × 76 mm height) and balls (9.6 mm diameter) were used. Contamination from the vial and balls was minimized by preparatory milling of the desired composition of powder mixtures for 30 minutes. After the cleaning, three grams of powder mixture was loaded in the vial with a weight ratio of powder : ball = 1 : 10. 1 wt % of stearic acid was added as a processing control agent. Samples were analyzed after preset milling time, that is, the vial was not exposed to the air until milling has finished. Pure Nb powders were milled for 45 hours to examine structural changes during the high energy milling, and used as a reference to understand structural features in the mechanically alloyed samples.

Structural evolution and phase transition during the MA process and annealing at elevated temperatures have been analyzed by X-ray diffraction (XRD). Monochromated CuK_α radiation was used at 40 kV and 25 mA. Step scanning (20 seconds duration at 0.04° intervals) between $2\theta = 27 - 48.5°$ was employed. Peak positions were determined by Gaussian curve fitting, and corrected refer to the internal Si standard. Microstructure and chemical composition of the milled powders were determined by a transmission electron microscope (TEM) equipped with energy dispersive x-ray spectroscope (Philips CM30). TEM specimens were prepared from the powder mixture with G1 epoxy (Gatan, Warrendale, PA), the cured mixture was polished, and final thinning for TEM observation was done by Ar ion milling.

Phase transformation of the MA powders upon heating was studied by a differential thermal analysis (DTA), and thermal behavior has been analyzed in connection with annealing treatments at 500, 850, 950 and 1200 °C for 2 hours in vacuum to understand the nature of endo- and exo-thermic peaks observed in DTA spectra.

3. Results and discussion

3.1. Mechanically alloyed powders

The X-ray diffraction patterns for the Nb-25%Al samples ball milled up to five hours are shown in Fig. 1a. The $(111)_{\mathrm{Al}}$ and $(110)_{\mathrm{Nb}}$ reflections overlap completely in the elemental mixture. Disappearance of Al reflections and broadening of Nb peaks are apparent from the early stage of milling. After three hours of milling, Al peaks seem to have disappeared completely and the $(110)_{\mathrm{Nb}}$ line is a dominant feature. Peak broadening and intensity decrease are somewhat significant, and peak shift towards to smaller diffraction angles has to be noticed after five hours of milling.

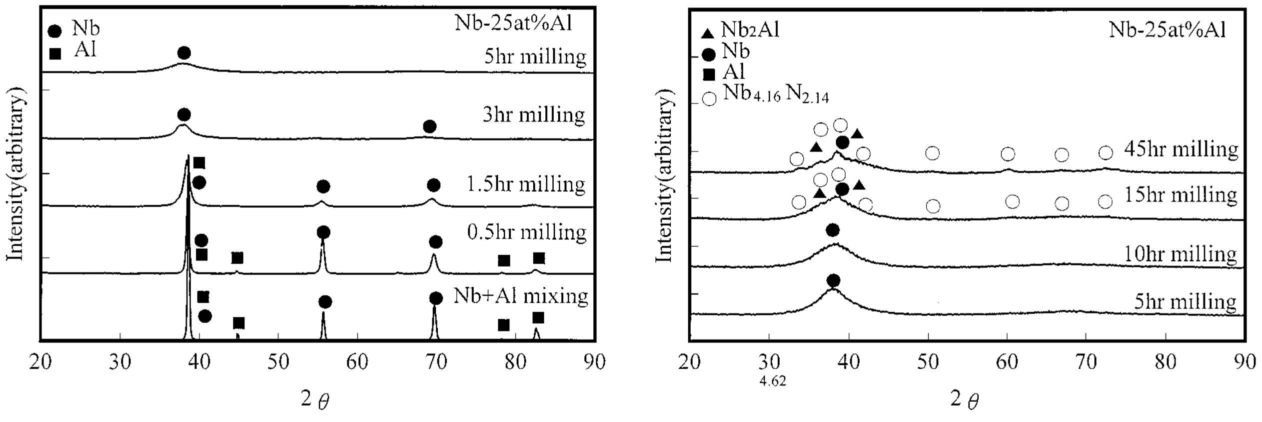
The disappearance of Al peaks in XRD spectra has been interpreted as a complete dissolution of Al in Nb [4, 6]. However, TEM observation shown in Fig. 2a revealed fine Al particles in the specimen after five hours of milling. It is clear that dissolution of Al has not been completed after five hours of milling and the disappearance of Al reflections in a XRD spectrum does not necessarily mean complete dissolution of Al in Nb.

Broadening of Nb peaks is due to decrease in the crystallite size and strain accumulation caused during the high energy ball milling. The change of the crystallite size and strain variance of the Nb is determined as a function of milling time using pure Nb powders as an internal standard, and are listed in Table I. After three hours of milling, the crystallite size has decrease to 6 nm in average, and this observation agrees with that of Tracy et al. [7].

XRD spectra after longer than 5 hours of milling are shown in Fig. 1b. After 10 hours, the $(110)_{\mathrm{Nb}}$ reflection is still the only noticeable feature wider beam broadening, which fact has been used as a proof of an amorphization. After 15 hours, the broad $(110)_{\mathrm{Nb}}$ peak becomes unstable and an indication of splitting into new peaks has appeared. The change has become clearer after 45 hours of milling: new peaks at higher diffraction angles have appeared. Electron diffraction

TABLE I Crystallite size and strain variance of the Nb-25at%Al alloy with milling time

Milling time (h)	Crystallite size (nm)	Strain variance
0.5	30	0.000371
1	31	0.000440
1.5	22	0.002701
3	6	0.002195



(a)

(b)

Figure 1 XRD spectra of the Nb-25at%Al sample after SPEX milling (a) up to 5 hours; and (b) up to 45 hours. Samples were mechanically alloyed during the indicated period without exposed in the air.

from the 15 hours sample (shown in Fig. 2b) shows both a halo of amorphous phase and ring patterns. It may be interpreted that the formation of the new phase started before the completion of amorphization. This analysis is different from previous work [6, 8], who interpreted the peak broadening around the $(110)_{\mathrm{Nb}}$ peak as an amorphization only.

The XRD spectrum after 45 hours of milling needs separate discussion. Except the splitting of the $(110)_{\mathrm{Nb}}$ peak into several reflections, another change is noticed around $2\theta = 50^\circ$, 60°, 67° and 74°. The change was confirmed by dark field TEM observation in Fig. 2c, and new nanocrystalline phase other than Nb or Nb-aluminides has formed. If the prominent peaks around $2\theta = 60^\circ$, 74° and split peaks around $2\theta = 40^\circ$ are considered, the planar distance ratio between the reflections corresponds to a face-centered cubic structure (FCC). However, if all traces at other positions are incorporated, XRD reflections fits better by a hexagonal structure. Possibility of NbC, NbN and NbO has been checked with the JCPDS file, and the new phase has been analyzed as the $\mathrm{Nb_{4.62}N_{2.14}}$. This nitride is commonly know as β-NbN, and is a meta-stable nitride with a trigonal lattice [9]. This analysis is different from earlier observation that the new phase after extended milling was identified as δ-NbN phase (or $\mathrm{Nb_4N_{3.92}}$) having FCC structure [6, 10].

It is appropriate that the sequence of structural evolution with milling time in the Nb-25at%Al composition is

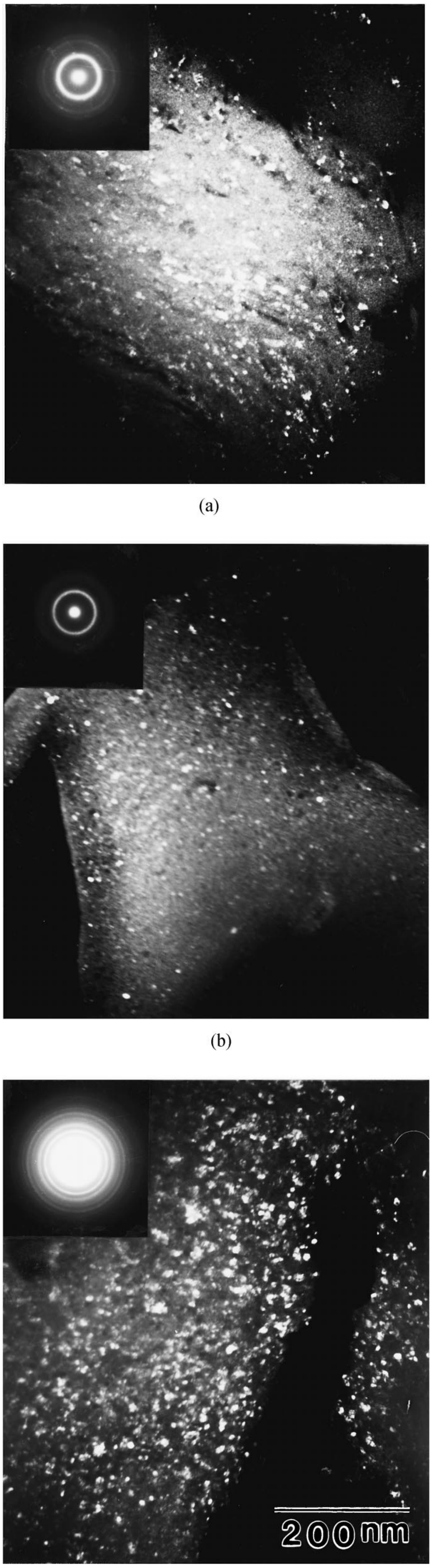
$$\begin{aligned}(\mathrm{Nb} + \mathrm{Al}) &\rightarrow \mathrm{Nb(Al)} + \mathrm{Nb} + \mathrm{Al}\\ &\rightarrow \text{amorphous} + \beta\text{-NbN}\end{aligned}$$

The slight increase in the peak intensity after 15 hours of milling could be interpreted as a transient state of the nitride formation. We believe that nitrogen from ambient atmosphere was incorporated during the milling process, and the metastable nitride might have started to form from the earlier stage of milling. This result is discussed in detail in later section with annealing behavior.

From peak positions of the $(110)_{\mathrm{Nb}}$ reflection, the lattice parameter of the Nb has been estimated, and the values are listed in Table II. The lattice parameter of Nb has increased to a value of 0.3343 nm after five hours of milling, and exhibited slightly decreasing tendency afterwards. They are all higher than that of pure Nb (i.e., 0.3307 nm), and current result agrees with an earlier observation by Hanada [11]. However, the reason for the increase is not obvious, because the lattice parameter Nb decreases with Al-content in Nb when Nb-Al samples are made by ingot metallurgy [11].

TABLE II Lattice parameter of Nb(Al) as a function of milling time

Milling time (h)	2θ-(110)	d-(110) (Å)	Lattice parameter (Å)
0	38.496	2.3385	3.3071
5	38.063	2.3641	3.3433
10	38.125	2.3604	3.3381
15	38.209	2.3554	3.3310



(a)

(b)

(c)

Figure 2 TEM dark field images and electron diffraction patterns of the Nb-25at%Al samples after (a) 5 hours; (b) 15 hours; and (c) 45 hours of milling. In the dark field images, presence of nano-sized aluminum, niobium and nitride, respectively, are clear.

3.2. DTA and annealing behavior

Fig. 3 shows DTA data of the specimens after milled for 5, 15 and 45 hours. In the figure, DTA of a Nb + Al mixture is given as a reference, where melting of Al and an exothermic peak indicating $NbAl_3$ formation appeared at 661.9 and 904 °C, respectively. Milled samples show endothermic reaction at about 400 °C: they are 417, 412.7 and 396 °C for the 5, 15 and 45 hours samples, respectively. XRD spectra from the ball milled powders annealed at 500 °C exhibited the same reflections as the MA powders, while the intensity ratio between $(110)_{Nb}$ and $(200)_{Nb}$ became closer to a normal value of 10/1. Therefore, the origin of these endothermic peaks is analyzed as the relaxation of stored energy form the heavily milled powders. As the amount of stored energy increased by a longer milling time, the temperature for the relaxation became lower accordingly.

Several exothermic peaks are noticed above 700 °C. There appear three peaks at 758, 836 and 935 °C for the 5 hours sample, two at 749.5 and 919.6 °C for the 15 hours sample and one at 829 °C for the 45 hours sample. Nature of the individual peaks are not clear at this time. However, the mechanically alloyed powders were annealed at 950 °C for two hours in vacuum to understand the eventual change. XRD spectra after the annealing are shown in Fig. 4 with that of the Nb + Al mixture annealed at the same temperature. In the Nb + Al mixture sample, reflections from Nb and $NbAl_3$ are dominant and an indication of Nb_2Al is observed, too. Nb powders have reacted with liquid Al to form $NbAl_3$ and Nb_2Al. Being the intermetallics are stable phases, the reactions should be exothermic.

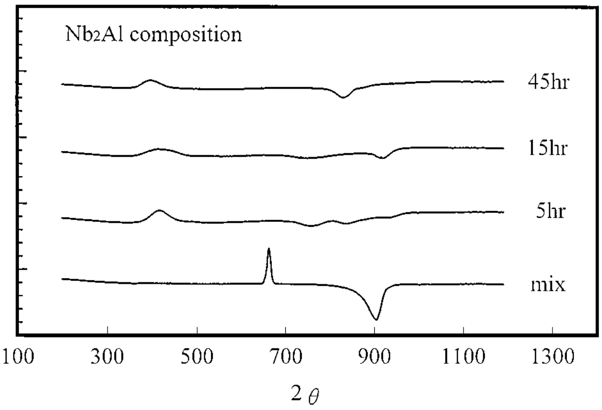


Figure 3 DTA data of the mechanically alloyed Nb-25at%Al samples with 5, 15 and 45 hours of milling with the Nb + Al mixture sample.

In the ball milled specimens, Nb has disappeared completely and Nb_2Al is the dominant feature with a new phase. There is no indication of Nb_3Al or $NbAl_3$. However, new phases also appeared with the Nb_2Al. The intensity for the new phase becomes progressively stronger as the milling time increases, that is, the new phase is most prominent in the sample with 45 hours milling. The peaks positions do not correlate with any Nb-aluminides documented in the JCPDS file. They correspond well to a hexagonal structure with close packed nature (i.e., HCP). Christensen synthesized the β-NbN by sintering of Nb powders in N_2 environment, and identified it as meta-stable nitride with trigonal structure [10]. With the finding in mind, the new phases appeared after 45 hours of milling has been reexamined, and the new phase has been analyzed as the β-NbN of $Nb_{4.62}N_{2.14}$ (or Nb_2N) fomular. This interpretation differs from earlier analyses by Hellstern *et al.* [4] and Peng *et al.* [6] and Pampus *et al.* [10] that the niobium nitride has been identified as FCC structure.

In order to clarify the role of nitrogen in the ambient environment, a Nb-25at%Al sample has been ball milled at Ar atmosphere for 15 hours and similarly annealed at 950 °C. Nitride formation after the milling was

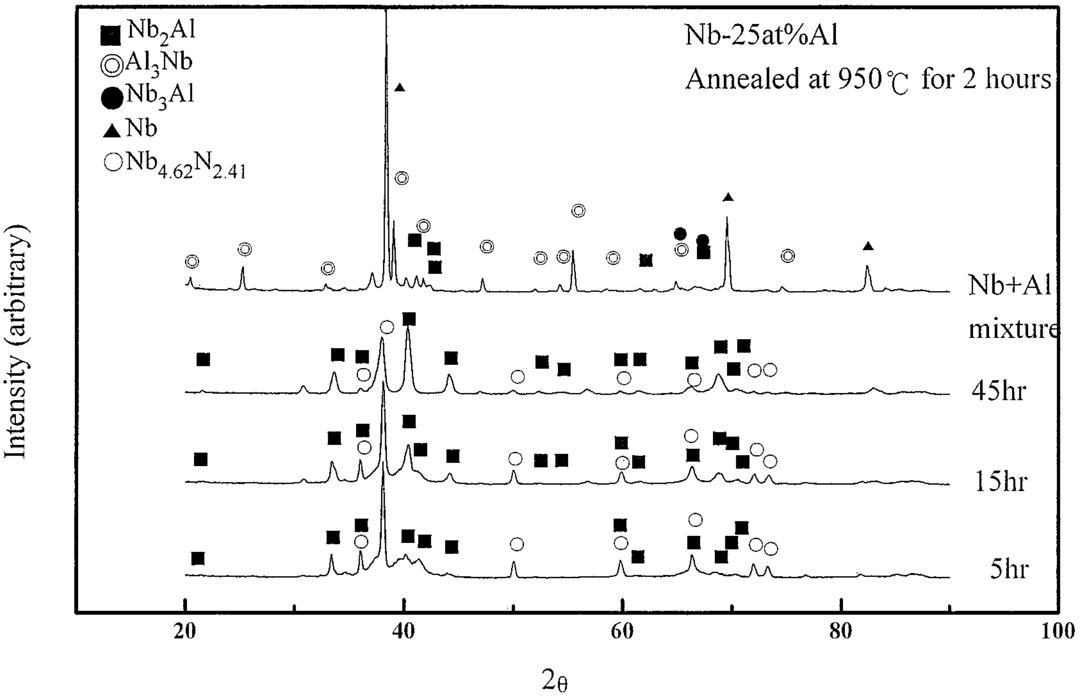


Figure 4 XRD spectra of the mechanically alloyed Nb-25at%Al samples after annealing at 950 °C for two hours. Nb_2Al and β-NbN have appeared after the annealing treatment.

not obvious as the one milled at ambient atmosphere. After the annealing, the Nb_3Al did form with Nb_2Al and the β-NbN. However, the intensity of the β-NbN was much smaller indicating that the nitride formation was reduced significantly. It is current understanding that even in the Ar atmosphere, nitrogen was not completely eliminated, and thus small amount of nitride has formed.

When the mechanically alloyed samples were annealed at 1200 °C, Nb_2Al was the dominant phase with less amounts of Nb_3Al and β-NbN. The volume fractions of Nb_3Al and β-NbN varied depending upon milling time in such a way that more Nb_3Al appeared in the samples with shorter milling time. Reflections from Nb_3Al did not present in the 45 hours sample, and β-NbN has appeared with Nb_2Al. Therefore, it is clear that long time milling is not appropriate for the synthesis of nanocrystalline Nb_3Al through mechanical alloying in an ambient environment.

As the annealing temperature increases, the mechanically alloyed structure changes according to following sequence.

$$\text{amorphous} + \beta\text{-NbN} \rightarrow \mathrm{Nb_2Al} + \beta\text{-NbN}$$
$$\rightarrow \mathrm{Nb_2Al} + \mathrm{Nb_3Al} + \beta\text{-NbN}$$

or

$$\rightarrow \mathrm{Nb_2Al} + \beta\text{-NbN}$$

4. Summary and conclusion

Structural evolution of the Nb-25at%Al (i.e., Nb_3Al) compositions during high energy ball milling and annealing at elevated temperatures are summarized as

(1) Structural evolution with milling time is

$$\mathrm{Nb} + \mathrm{Al} \rightarrow \mathrm{Nb(Al)} + \mathrm{Nb} + \mathrm{Al} \rightarrow \text{amorphous} + \beta\text{-NbN}$$

Complete dissolution of Al in Nb has not completed before amorphization started, and nitrogen from ambient atmosphere were incorporated during the milling process, and the metastable nitride of $Nb_{4.62}N_{2.14}$ (i.e., β-NbN) has started to form from the early stage of milling.

(2) The lattice parameter of Nb increased significantly during the mechanical alloying. It became 3.3433 Å after 5 hours of milling, and the value is much higher than that of pure Nb (e.g., 3.3071 Å). The increase cannot be interpreted by dissolution of Al only.

(3) Upon annealing at the mechanically alloyed Nb-25at%Al sample at 950 °C, Nb_2Al was the dominant phase with β-NbN and Nb_3Al was not observed if the nitride has formed during mechanical alloying. Structural evolution during annealing is as follows,

$$\text{amorphous} + \beta\text{-NbN} \rightarrow \mathrm{Nb_2Al} + \beta\text{-NbN}$$
$$\rightarrow \mathrm{Nb_2Al} + \mathrm{Nb_3Al} + \beta\text{-NbN}$$

or

$$\rightarrow \mathrm{Nb_2Al} + \beta\text{-NbN}$$

depending upon milling time in ambient atmosphere. Nb_3Al has appeared only when samples with short time milling were heated up to 1200 °C.

In conclusion, milling environment is an important factor determining the structural features appearing during mechanical alloying and annealing of the Nb-15at%Al. Nitrogen plays a critical role. If nitrogen is present, the formation of Nb_3Al is retarded significantly or prevented. Therefore, it is clear that long time milling is not appropriate for the synthesis of nanocrystalline Nb_3Al through mechanical alloying in an ambient environment.

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