



Investigation of in-situ synthesis of NbAl₃/Al₂O₃ nanocomposite by mechanical alloying and its formation mechanism

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ABSTRACT

The present study was carried out to synthesize NbAl₃/Al₂O₃ intermetallic matrix nanocomposite by mechanical alloying (MA) using Nb₂O₅ and Al as raw materials. This nanocomposite was produced through a mechanochemical reaction between Nb₂O₅ and Al. The structural changes of powder particles during mechanical alloying were studied by X-ray diffractometry and scanning electron microscopy techniques. It was found that the reaction between Al and Nb₂O₅ takes place in an explosive mode after about 450 min of milling time. The milled powder had a microstructure consisting of nanocrystalline NbAl₃ base adjacent to Al₂O₃ particles with a nanoscale grain size. At longer milling times, no changes were observed, except peaks broadening due to the decreasing in crystallite size and increasing in lattice strain. After 15 h of milling time, average crystallite size of NbAl₃ and Al₂O₃ were about 8 and 13 nm, respectively. Heat treatment of powder mixture milled for 15 h showed a good thermal stability for this nanocomposite.

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1. Introduction

Intermetallic compounds have been the focus of significant research and development efforts during the last years. Some intermetallic compounds such as Fe₃Al, NiAl, TiAl and NiTi are being recognized as potential high temperature structural materials. Among intermetallic compounds, niobium aluminides are so important and attractive. Three intermetallic compounds are present in the Nb–Al binary system including Nb₃Al (A15 structure, Cr₃Si type), Nb₂Al (D8b structure, σ–CrFe type) and NbAl₃ (DO22 structure, TiAl₃ type) [1]. Niobium aluminides are of interest as candidates for high temperature structural materials due to their high melting point, high elastic modulus, and low densities compared with Ni-based superalloys [2]. Among various compounds in the Al–Nb system, NbAl₃ with its high melting point (1878 K), low density (4.54 g/cm³), is attractive as a potential material for high temperature applications [3]. These applications include its use in turbine blades in aircraft engines or in stationary gas turbines [4]. However, despite its attractive features, its use is limited by two shortcomings: inadequate ductility at room temperature [5,6] and a relatively unsatisfactory oxidation resistance at temperatures above 973 K [7–10]. So, for optimization of room temperature toughness and high temperature strength, microstructural modifications are required. For these reasons it has

been recognized that intermetallic matrix composites (IMCs) may be appropriate materials for structural applications, replacing in some cases intermetallics [11]. In the last few years numerous IMCs such as NiTi/Al₂O₃, NiAl/Al₂O₃, (Fe,Ti)₃Al/Al₂O₃ and Fe₃Al/Al₂O₃ have been synthesized by different investigators [12–15]. On the other hand, demand for novel materials with superior properties for aerospace applications has prompted research for synthesizing nanocrystalline materials. A number of papers [16–18] have reported many unique properties associated with nanocrystalline materials, such as the enhanced ductility and diffusivity compared with ordinary materials. In other words, another way to increase ductility in intermetallics is to synthesize fine-grain microstructure [19,20].

Fabrication of intermetallic matrix composites has been conducted by a variety of methods, e.g., self-propagating high temperature synthesis (SHS), reactive hot press [21] and mechanical alloying (MA) [22]. Among these methods, MA technique is well known for synthesis of compounds and nanocomposites using the mechanochemical reactions. The mechanically driven chemical reduction process (mechanosynthesis) has a number of advantages over the conventional metal processing techniques. It enables the reduction of metal oxides and halides directly to pure metals or alloys without first having to convert the oxides to pure metals and then to the desired alloy. Furthermore, mechanical alloying can provide the means to substantially increase the kinetics of reduction reactions. As a consequence, reactions that normally require high temperatures will occur at lower temperatures during MA without any externally applied heat [22]. Moreover, combustion synthesis

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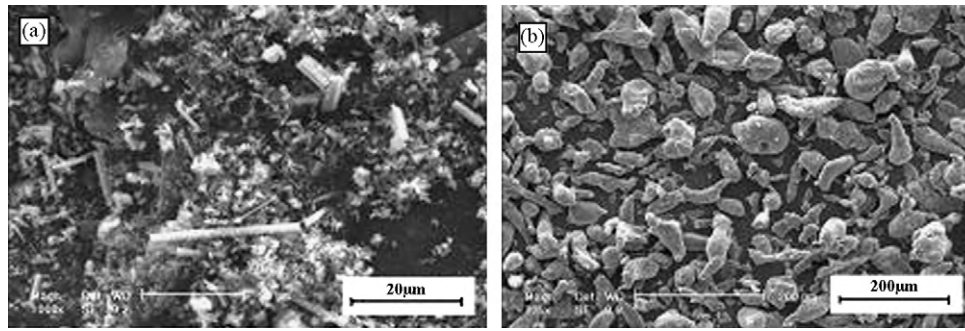


Fig. 1. SEM morphology of initial powders: (a) Nb₂O₅; (b) Al.

represents an in-situ processing technique for the preparation of composite materials with interpenetrating phase microstructures and improved properties [23]. Especially, both the reactions for the reinforcement and matrix formation are exothermic in the preparation of IMCs [24].

In choosing a suitable combination of matrix and reinforcement, compatible thermal expansion coefficients are required to reduce the thermal contraction stress, which can lead to cracking of the composite and severe degradation of the mechanical properties [25,26]. Al₂O₃ has a combination of desirable properties, such as low density, high specific strength and high modulus [21] which can provide stiff ceramic inclusions introduced into an intermetallic matrix, such as NbAl₃, enhancing the mechanical properties and thermal stability of the composite.

Unfortunately, there has been no study concerning the mechanochemical formation mechanism of niobium aluminide-based nanocomposites. In this paper, the feasibility of using displacement reactions to process niobium–aluminide matrix nanocomposite with an Al₂O₃ reinforcing phase is evaluated. Details of the processing steps are discussed and microstructural characterization is performed.

2. Materials and methods

2.1. Materials

Mixtures of pure aluminum (purity >99%, particle size ≤ 45 μm) and Nb₂O₅ powders (purity >99.5%, particle size ≤ 15 μm) in the stoichiometric ratio of 49 wt.% Al were used as starting materials. Fig. 1 shows the morphology of the initial powders. Al powder has a random morphology while Nb₂O₅ spongy. No process control agent (PCA) was used as the powder mixture contains 51 wt.% brittle Nb₂O₅.

2.2. Milling

Milling was carried out at room temperature using a planetary high-energy ball mill (Fritch pulverisette5 type). High chromium–carbon hardened steel vial (57 mm diameter and 76 mm height) containing the powders and the balls (15 mm diameter) is fixed onto a rotating disc and rotates in the opposite direction to that of the larger platform. The rotation speed of the vial and the platform were fixed at 350 and 175 respectively rpm. The mass of powder charge was 10 g and the weight ratio between steel balls and the powder charge was controlled about 15:1 in all cases. The powder sample and milling balls were loaded into the vial, which was filled with Ar gas to avoid air contamination. The rise in vial temperature was measured with an external thermocouple.

2.3. XRD analysis and crystallite size measurement

X-ray diffractometry was used to follow the structural changes of powders after milling and annealing. A Philips diffractometer (40 kV) with Cu K_α radiation (λ = 0.15406 nm) was used for XRD measurements. The XRD patterns were recorded in the 2θ range of 30–90° (step size 0.05° and time per step 0.5 s). The crystallite size and internal strain for Nb₂O₅, Al, NbAl₃ and Al₂O₃ were evaluated using the Williamson–Hall formula [27]:

$$\beta \cos \theta = \frac{0.9\lambda}{D} + 2\varepsilon \sin \theta \quad (1)$$

where θ is the Bragg diffraction angle, D is the average crystallite size, ε is the average internal strain, λ is the wavelength of the radiation used and β is the diffraction

peak width at half maximum intensity. The average internal strain can be estimated from the linear slope of β cos θ versus sin θ, and the average crystallite size can be estimated from the intersect of this line at sin θ = 0. The shape of both contributions coming from the refinement and strain was assumed Gaussian.

2.4. Microstructural observation

The morphology of the milled powders was analyzed by scanning electron microscopy (SEM) using a Philips XL30 at an accelerating voltage of 30 kV. Powder samples were fixed in small quantities on a sample holder by graphite sticky tape.

2.5. Heat treatment

For heat treatment of powders, the samples were placed in Al₂O₃ pans and heated in a tube furnace with dynamic Ar atmosphere at 1073 K for 60 and 90 min.

3. Results and discussion

3.1. Phase evolution and reaction mechanism

NbAl₃/40 vol.%Al₂O₃ nanocomposite can be synthesized by a displacement reaction during ball milling of Al with 51 wt.% Nb₂O₅ according to the following reaction:



$$\Delta G^\circ = -2982.22 + 0.94823T(\text{kJ/mol})[28] \quad (3)$$

During milling at ambient temperature reaction (2) can thermodynamically occur due to its negative free energy change. ΔH° for this reaction is also negative, indicating that the Al–Nb₂O₅ reaction is exothermic. Fig. 2 shows the XRD patterns of powder mixture after different milling times. The diffraction patterns of initial powder mixture show several peaks corresponding to Al and Nb₂O₅. XRD patterns of powder mixture after 5 h of milling

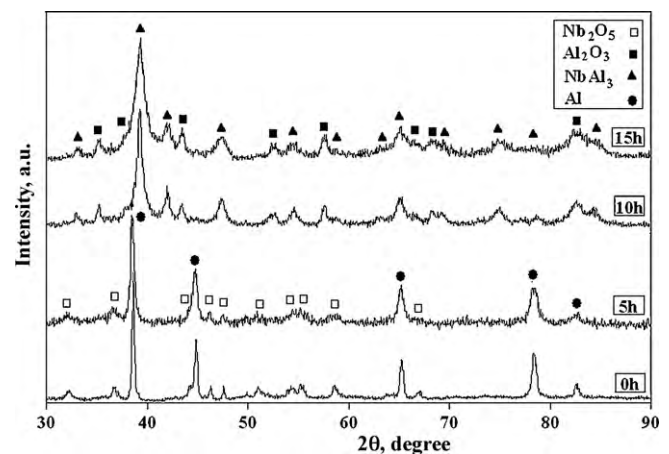


Fig. 2. XRD patterns of Al–Nb₂O₅ powder mixture after 0, 5, 10 and 15 h of milling.

time (prior to combustion reaction) was identified as a mixture of Al and Nb₂O₅ indicating that ball milling up to 5 h had no effect on as-received powder mixture except broadening of Bragg peaks due to the nanostructure formation and the enhancement of lattice strain. Crystallite size and mean lattice strain of Nb₂O₅ and Al after 5 h of milling time were calculated to be 77 nm, 0.8% and 81 nm, 0.4% respectively. Reducing the crystallite size to nanometer range and increasing the defect densities increase the reaction rate by providing short circuit diffusion paths [29]. At longer milling times the activation energy required for reaction between Nb₂O₅ and Al is provided through mechanical activation and this reaction occurs. So, after 10 h of milling time the NbAl₃ and Al₂O₃ peaks are present in the XRD pattern. In other words, when the milling time was increased to about 10 h, reaction (2) occurred. As a result, the released heat from exothermic reaction (2) provides the activation energy for NbAl₃ formation at the same time.

Depending on the milling conditions, two entirely different reaction kinetics are possible:

- (1) the reaction may extend to a very small volume during each collision, resulting in a gradual transformation, or
- (2) if the reaction enthalpy is sufficiently high, a self-propagating combustion reaction can be initiated [22].

T_{ad} is known as a thermodynamic parameter to predict the modality of mechanochemical reactions (gradual/combustion). A value of $T_{ad} > 1800$ K is generally considered to be the minimum necessary temperature for the occurrence of self-propagating combustion in a thermally ignited system [30]. In contrast, Schaffer and McCormick [29] showed that a value of $T_{ad} > 1300$ K is adequate for the sudden occurrence of displacement reaction during ball milling. The value of T_{ad} for reaction (2) was calculated according to the following calculations:

$$-\Delta H = \sum \left(n_p \int_{298}^{T_m^p} C_{ps}^p dT \right) + \sum (n_p \Delta H_m^p) + \sum \left(n_p \int_{T_m^p}^{T_{ad}} C_{pl}^p dT \right) \quad (4)$$

where ΔH is the enthalpy change of reaction, n_p the molar fractions of products, T_m^p the melting point, C_{ps}^p the heat capacity in solid phase, C_{pl}^p the heat capacity in liquid phase and ΔH_m^p is the enthalpy of fusion of products. The adiabatic temperature, T_{ad} , for this reaction (2798 K), is higher than the critical value of 1300 K or even 1800 K. It is therefore expected that a combustion reaction takes place during milling of Al and Nb₂O₅ powder mixture. This can be promoted by the dynamically maintained high reaction interface areas [31]. It is proposed that the ignition temperature decreases with increasing milling time as a result of microstructure refinement, mechanical activation, and the momentary temperature rise resulting from milling media collisions [32]. In order to determine the modality of reaction (2) experimentally, the vial temperature was measured during ball milling. As can be seen in Fig. 3, in the initial stages of milling, the vial temperature gradually increased as a result of heat generated by collisions of balls until a steady-state value was achieved. An abrupt increase of temperature to 335 K ($\Delta T = 35$) occurred after about 450 min of milling time, indicating the occurrence of the combustion reaction between Nb₂O₅ and Al. The temperature then decreased rapidly to the steady-state value.

The local heat generation can lead to the formation of crystalline Al₂O₃ rather than the amorphous Al₂O₃ [15]. It should also be noted that no new phase was developed on XRD patterns even after long milling times. Ball milling for 15 h led to broadening of NbAl₃ and Al₂O₃ diffraction peaks as a result of two effects; refinement of

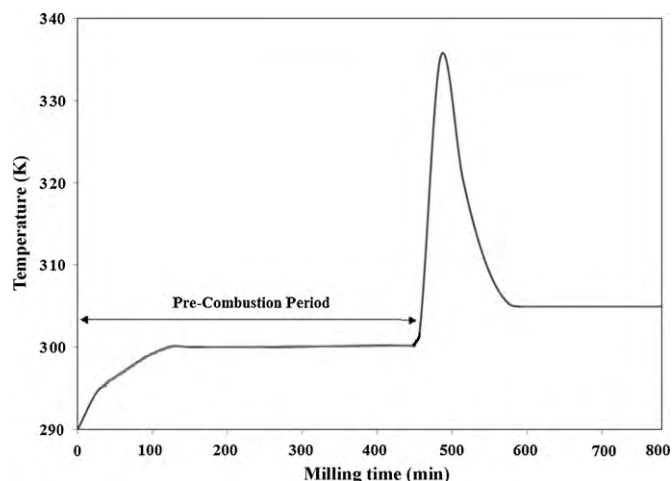


Fig. 3. Variation of vial temperature versus time during milling of Al–Nb₂O₅ powder mixture.

Table 1
Crystallite size and internal strain of powder particles at different conditions.

Condition	Crystallite size (nm)		Internal strain (%)	
	NbAl ₃	Al ₂ O ₃	NbAl ₃	Al ₂ O ₃
10h MA	10	16	0.25	0.20
15h MA	8	13	0.40	0.30
15h MA + 60 min annealing	11	19	0.18	0.15
15h MA + 90 min annealing	15	22	0.15	0.11

crystallite size as well as enhancement of its internal strain. Both effects are caused by severe plastic deformation of powder particles upon impact force of colliding balls during milling process [33–35]. Crystallite size and lattice strain of Al₂O₃ and NbAl₃ at different conditions are presented in Table 1.

3.2. Thermal stability

Nanocrystalline structures are thermodynamically unstable because of the large excess free energy stored in their grain boundaries. Significant grain growth was observed in several nanocrystalline materials [36,37]. The study of thermal behavior of nanostructured materials is therefore important with respect to the possible applications.

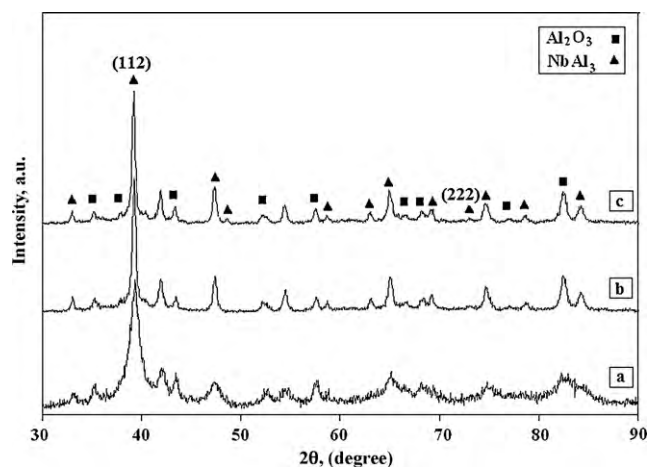


Fig. 4. The XRD patterns of Nb₂O₅/Al as-milled powders for 15 h (a) before annealing, (b) after annealing at 1073 K for 60 min, and (c) after annealing at 1073 K for 90 min.

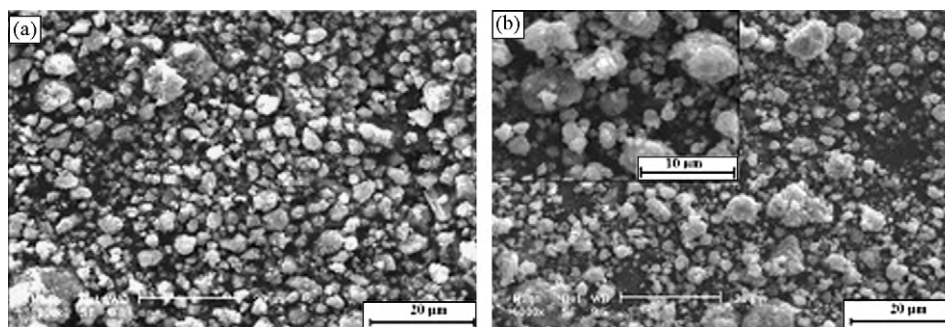


Fig. 5. Morphology of powder particles after (a) 2 h, and (b) 10 h of milling time.

Thermal stability of NbAl₃–Al₂O₃ nanocomposite structure was investigated by annealing of milled powders at 1073 K for 60 and 90 min. The XRD patterns of samples milled for 15 h and after subsequent annealing are shown in Fig. 4. The width of XRD peaks of NbAl₃ and Al₂O₃ decreased and their intensity increased after annealing due to the reduction of lattice strain as well as grain growth. The NbAl₃ and Al₂O₃ crystallite size after annealing for 60 and 90 min reached 11 and 19 nm, 15 and 22 nm, respectively, see Table 1. Considering the grain growth as a criterion for thermal stability, it can be concluded that the NbAl₃/Al₂O₃ nanocomposite prepared in this work shows suitable thermal stability. Among the three intermetallics in the Al–Nb system, NbAl₃ has the highest negative enthalpy of formation so that complete disordering of the NbAl₃ is energetically unfavorable during mechanical alloying [3]. It can be suggested that NbAl₃ changes to a metastable partially disordered state on further continued milling. But, due to the following heat treatment, some new NbAl₃ peaks are formed and other peaks become clearly stronger. This reason and decrease in lattice strain can be interpreted as the occurrence of an order–disorder transformation in NbAl₃ phase.

The relative long-range order (LRO) parameter, *S*, was determined by a comparison of the relative intensities of superlattice–fundamental pairs of peaks (2 2 2/1 1 2) of milled and/or annealed powders with respect to the homogenized reference material according to the equation given by Bakker et al. [38].

$$S = \sqrt{\frac{(I_S/I_F)_{dis}}{(I_S/I_F)_{hr}}} \quad (5)$$

where $(I_S/I_F)_{dis}$ and $(I_S/I_F)_{hr}$ are the intensities of the superlattice reflection taken relative to the fundamental line for the disordered (e.g., milled) (dis) and homogenized reference (hr) powder, respectively. Using Eq. (5), LRO was obtained as 0.75 and 0.8 after annealing for 60 and 90 min, respectively. It can be interpreted that annealing for 90 min leads to lower density of lattice defects and therefore more ordering in structure. The actual volume content of Al₂O₃ based on the XRD patterns of specimen milled 15 h and annealed for 90 min at 1073 K, using “Direct comparison method” [39]. The calculated value was 33 vol.% for alumina which is comparable to the nominal value (40 vol.%).

3.3. Morphological analysis

The changes in morphology of powder particles during milling process are shown in Fig. 5. In all milling stages the powder particles were irregular in shape. In the early stages of milling, Nb₂O₅ was mixed with Al at the micrometer level and a homogenous and active composite was formed. Therefore, ball milling up to 120 min led to the refinement of powder particles and the average size of powder particles before combustion reaction reached about 2 μm (Fig. 5a). Then, the reaction between Al and Nb₂O₅ took place abruptly after about 450 min of milling time (Fig. 4) and as seen

from Fig. 5b after this time, the size of powder particles increased again. In fact, exothermic reaction between Al and Nb₂O₅ increases the temperature locally and causes the particle size to grow.

4. Conclusions

NbAl₃–Al₂O₃ nanocomposite powder with 40 vol.% Al₂O₃ was directly synthesized by mechanochemical reaction between Nb₂O₅ and Al powders using high-energy ball milling. Measurement of vial temperature, XRD analysis, and morphology changes during ball milling confirmed the occurrence of combustion reaction which led to the formation of NbAl₃ intermetallic compound and Al₂O₃ phase. Prior to combustion reaction, the Nb₂O₅ and Al powder particles attained a nanocrystalline structure which promoted the Nb₂O₅–Al reaction by providing high diffusivity. It was found that after 15 h of milling time, average crystallite sizes of NbAl₃ and Al₂O₃ were about 8 and 13 nm, respectively. Thermal behavior results showed that nanocomposite powders were stable during heating.

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