International Journal of Minerals, Metallurgy and Materials
Volume 26, Number 3, March 2019, Page 345
https://doi.org/10.1007/s12613-019-1743-7

Synthesis of a $NiTi_2$–AlNi–Al_2O_3 nanocomposite by mechanical alloying and heat treatment of Al–TiO_2–NiO

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(Received: 19 April 2018; revised: 3 October 2018; accepted: 8 October 2018)

Abstract: The aim of the present study was to investigate the phases formed during ball milling of Al–TiO_2–NiO. For this purpose, a mixture of Al–TiO_2–NiO with a molar ratio of 6:1:1 was used. Characterization of the milled powders by X-ray diffraction, differential thermal analysis, field-emission scanning electron microscopy, and transmission electron microscopy showed the formation of nanocrystalline $NiTi_2$ along with AlNi. A thermodynamical investigation confirmed that NiO was reduced by Al during ball milling, which consequently promoted TiO_2 reduction and the formation of $NiTi_2$. Al is capable of reducing NiO either during ball milling or at temperatures above the melting point of Al; by contrast, TiO_2 can be reduced by Al only by milling.

Keywords: mechanical alloying; $NiTi_2$–AlNi; nanocomposite; reaction mechanism

1. Introduction

Metallic materials such as Al and Cu need to be strengthened through incorporation into composites with hard ceramics or into intermetallic compounds (IMCs) to enhance their wear resistance and hardness [1–2]. Oxides such as Al_2O_3 cannot be used directly as starting materials for producing metal-matrix composites (MMCs) [3]. Al_2O_3 is used as a reinforcement particle in soft metallic matrixes such as Al, Mg, and Ni [4–5]. Mechanical alloying can be used to produce nanocrystalline compounds in the solid state through *in situ* reactions [3,6]. Both MMCs and IMCs can be produced by milling via a chemical reaction between starting powders [7].

The Al–Ni–Ti system is an attractive system for preparing IMCs via mechanical alloying [8]. Ball milling promotes reactions at low temperatures that would otherwise require high temperatures [3,9]. Thus far, Ni–Ti alloys have been studied because of their attractive mechanical and chemical properties [10]. For example, NiTi is increasingly being used as a shape-memory alloy in medical applications [10] and $NiTi_2$ cladding offers excellent wear resistance and corrosion protection on a Ti substrate [11–12]. The formation of *in situ* products by reduction of metallic oxides with Al has attracted extensive attention over the past decade [9,13–16]. Conventional solidification methods cannot be used to produce certain alloys because of constraints in phase equilibria [17]. However, mechanical alloying is considered a good potential method for producing such alloys.

Most previous studies carried out on mechanical alloying of Al–Ni–Ti have involved ball milling of a metal oxide with Al powder. Given the different properties of various IMCs, in the present study, we focus on ball milling of TiO_2, NiO, and Al powders. The aim of this study is to investigate the formation of Al–Ti, Al–Ni, and Ni–Ti IMCs during ball milling and a subsequent heat treatment. The mechanism of phase formation is also investigated and analyzed.

2. Experimental

The starting powders used in this study were TiO_2 powder (99.5% purity, average particle size of 10 μm), Al powder (99.9% purity, average particle size of 50 μm), and NiO

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powder (99.5% purity, average particle size of 50 μm). The relative amounts of each powder were selected in accordance with Eqs. (1) and (2):

$$5Al + 3NiO = 3AlNi + Al_2O_3,$$
$$\Delta G_T^{\ominus} = -1310847 - 92.24T \text{ J/mol} \quad (1)$$
$$13Al + 3TiO_2 = 3Al_3Ti + 2Al_2O_3,$$
$$\Delta G_T^{\ominus} = -738897 - 234.77T \text{ J/mol} \quad (2)$$

For mechanical alloying, a planetary ball mill was used; the vial and balls were made of hard chromium steel, and the operation was carried out at room temperature. Three ball sizes were used: small (0.4 mm), medium (0.7 mm), and large (10 mm). The powder mixture was ball milled under an Ar atmosphere and at a rotation speed of 350 r/min for 30 h. The ball-to-powder mass ratio was 10:1. No agent control was used. For differential thermal analysis (DTA), a Reometric STA 503 differential thermal analyzer with a temperature accuracy of ± 0.1°C was used, with the sample under Ar supplied at a rate of 60 mL/min. Two powders—as-mixed and 30-h-ball-milled powders—were heated at a rate of 10°C/min to 1000°C. X-ray diffraction (XRD) was used to identify the phases formed after ball milling as well as after heat treatment.

Field-emission scanning electron microscopy (FESEM) was used to characterize the morphology and grain size of the ball-milled samples. A Philips CM200 transmission electron microscope was used to investigate the nanocrystallinity of ball-milled powders by selected-area diffraction (SAD) and bright-field imaging.

3. Results and discussion

3.1. Ball milling of the powders

FESEM images of the as-mixed powder and the 30-h-ball-milled powder are shown in Figs. 1(a) and 1(b), respectively. The refinement and agglomeration of particles is observed in Fig. 1(b). This phenomenon is attributed to the repeated welding and fracturing of the powders during ball milling [18].

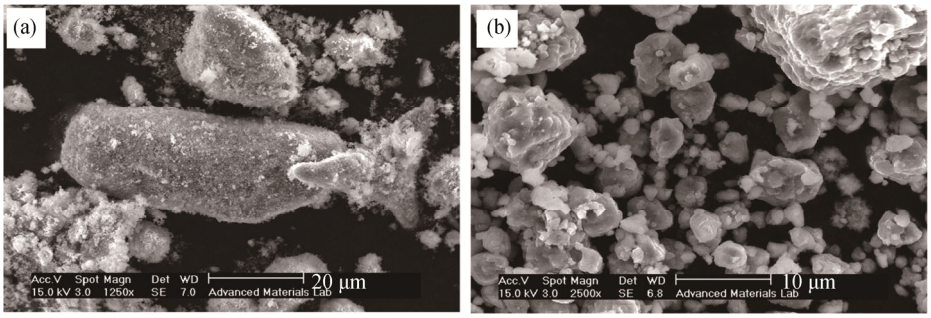

Fig. 1. FESEM images of (a) the starting powder mixture and (b) the ball-milled powder.

Fig. 2 shows the XRD patterns of the powder after 30 h of ball milling. The main phases formed were AlNi, $NiTi_2$, and Al_2O_3. This result implies that, in addition to Eq. (1), other reactions occurred during ball milling. To explain this observation, we consider the Gibbs free energy changes of the reactions that lead to the formation of $NiTi_2$ from the initial reactants. If Al is assumed to function as a reducing agent, the following reaction can be considered for producing $NiTi_2$:

$$10Al + 6TiO_2 + 3NiO = 3NiTi_2 + 5Al_2O_3,$$
$$\Delta G_T^{\ominus} = -2247647 - 126.77T \text{ J/mol} \quad (3)$$

The Gibbs free energy changes for Eqs. (1) to (3) are shown in Fig. 3. Eq. (3) is energetically more favorable than Eqs. (1) and (2). Therefore, the formation of $NiTi_2$ during ball milling is thermodynamically favored over the formation of other phases because of its more negative Gibbs free energy changes.

The formation of Al_2O_3 in Eq. (3) implies that a reduction occurs during ball milling. Ying *et al.* [7] reported that no reaction occurred between Al and TiO_2 even after 60 h of ball milling. Also, Udhayabanu *et al.* [16] reported that the reduction of NiO by Al and the formation of AlNi occur during ball milling of Al–NiO, although the reaction is incomplete. As shown in Fig. 2, some peaks of AlNi appear in the XRD pattern of the ball-milled sample. These results indicate that an intermediate reaction occurred, whereby AlNi was produced. That is, Eq. (1) occurred before Eq. (3). Therefore, $NiTi_2$ formed as a result of Eq. (1) and the following reaction:

$$5Al + 3NiAl + 6TiO_2 = 4Al_2O_3 + 3NiTi_2 \quad (4)$$

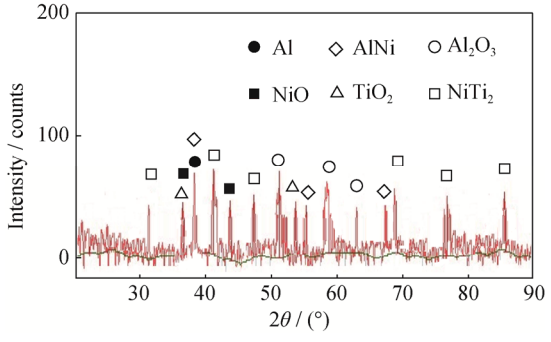

Fig. 2. XRD pattern of the 30-h-ball-milled powder.

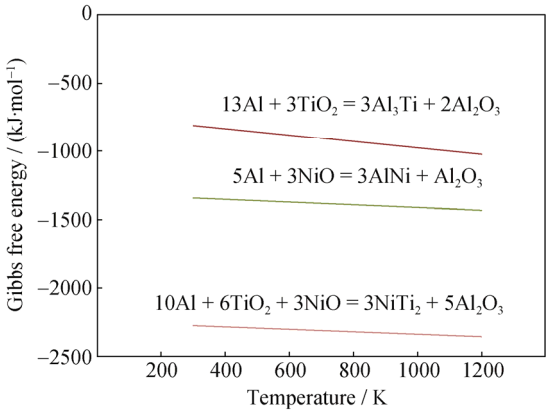

Fig. 3. Variation of the Gibbs free energy of different reactions as a function of temperature.

Notably, the high enthalpy of Eq. (1) might strongly contribute to the reduction of TiO_2. No intermediate phase formed between Al and Ti, and the final products Al_2O_3 and $NiTi_2$ formed directly from TiO_2 according to Eq. (4). The absence of AlNi would promote the reduction of TiO_2 and the formation of IMCs between Al and Ti [19–20]. The explained mechanism is summarized in Fig. 4. The procedure can be explained as follows: During the initial stages of ball milling, NiO is partially reduced and reacts with Al according to Eq. (1). Thereafter, TiO_2 and the products from the previous stage react according to Eq. (4), leading to the formation of $NiTi_2$. The heat generated by Eq. (4) promotes NiO reduction according to Eq. (1), which in turn provides one of the prerequisites for reaction (4); that is, Eqs. (1) and (4) are interdependent. Eq. (4) proceeds until the TiO_2 is consumed. Upon termination of Eq. (4), the loss of this heat source results in excess amounts of Al and NiO remaining in the system; their incomplete reaction leads to the formation of AlNi. The transmission electron microscopy (TEM) images and corresponding SAD pattern of the 30-h-ball-milled powder are shown in Figs. 5(a) and 5(b), respectively. The existence of several continuous ring patterns and the absence of any preferred orientation imply that the powder is nanocrystalline.

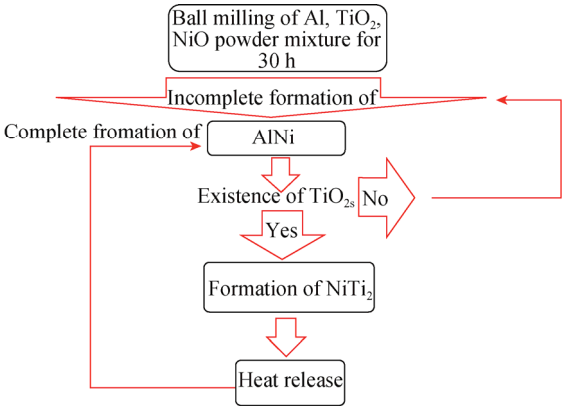

Fig. 4. Summary of the mechanism of the reactions during ball milling of Al–TiO_2–NiO.

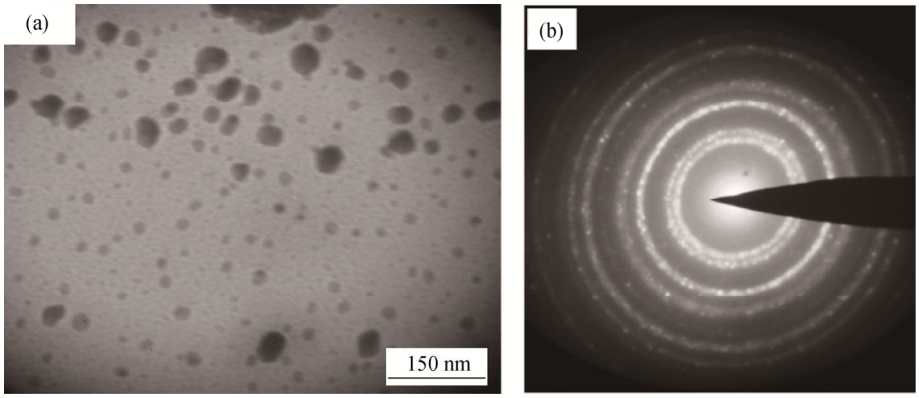

Fig. 5. TEM images (a) and corresponding SAD pattern (b) of the 30-h-ball-milled powder.

3.2. DTA analysis

To assess the thermal stability of $NiTi_2$ and investigate other possible reactions at higher temperatures, we heated the ball-milled powder to 1000°C using the DTA technique; the results are shown in Fig. 6(a). The DTA analysis of the as-mixed powder is shown in Fig. 6(b). The DTA thermogram of the ball-milled powder shows exothermic peaks at 820°C and 950°C. The XRD results of the ball-milled powders heat treated at 820 and 950°C are shown in Fig. 7(a) and 7(b), respectively. Some new peaks corresponding to AlNi appeared. The reduction of the remaining NiO by Al occurred at 820°C, which is slightly higher than the temperature reported by Olezsak [13]. This difference is attributable to dilution of the system by other phases. Given the excess amount of Al and NiO that remained after ball milling, we concluded that Eq. (1) was completed at 820°C. No considerable difference is observed between Fig. 7(a) and 7(b). The peak at 950°C in the DTA thermogram is attributed to recrystallization of the Al_2O_3.

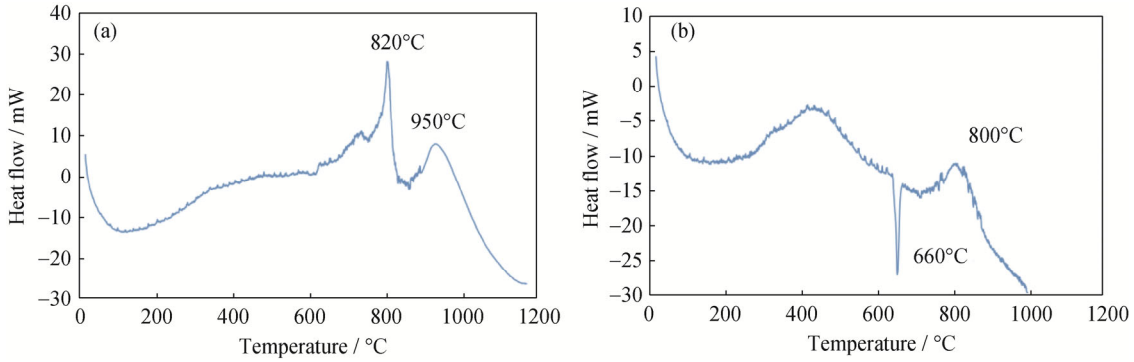

Fig. 6. DTA thermograms of (a) the ball-milled and (b) the as-mixed powders.

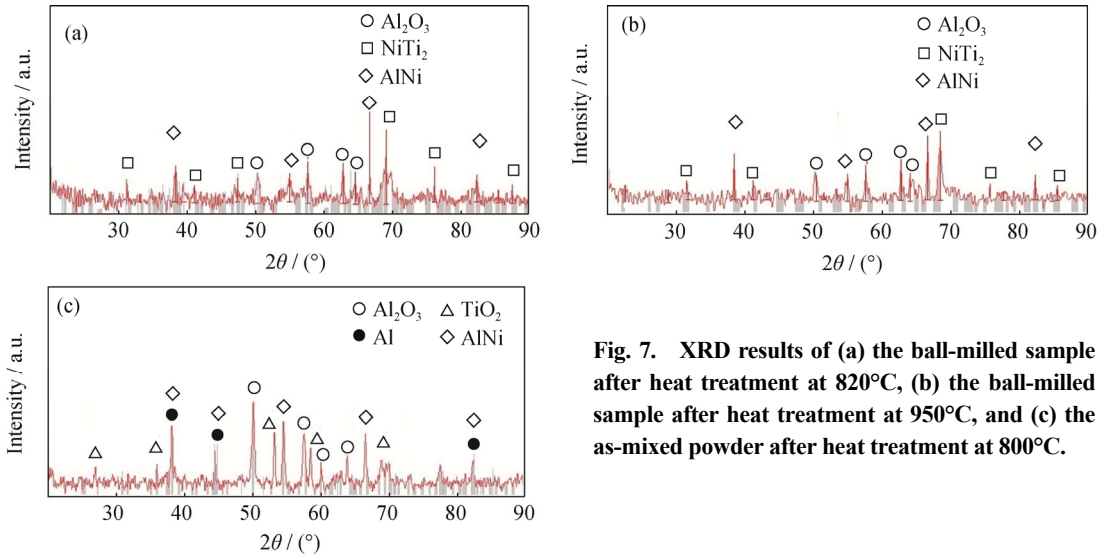

Fig. 7. XRD results of (a) the ball-milled sample after heat treatment at 820°C, (b) the ball-milled sample after heat treatment at 950°C, and (c) the as-mixed powder after heat treatment at 800°C.

The DTA results for the as-mixed powders heat treated at temperatures as high as 1000°C show an endothermic peak at 650°C and an exothermic peak at 800°C. The endothermic peak corresponds to the melting of Al. The XRD results for the sample heat treated at 800°C (Fig. 7(c)) indicate the presence of AlNi, TiO_2, and Al_2O_3. Accordingly, we concluded that, in the as-mixed powder, Eq. (1) occurred after the Al melted, whereas TiO_2 did not react.

Given the aforementioned results, Al can reduce NiO either during ball milling or after melting of Al, resulting in the formation of AlNi. However, as noted, the formation of AlNi is incomplete during ball milling. The production of $NiTi_2$ provides the heat necessary to produce AlNi during ball milling. The TiO_2 phase is reduced by Al only during ball milling, whereby $NiTi_2$ is formed and all of the TiO_2 is consumed during ball milling.

4. Conclusions

The Al–TiO_2–NiO powder mixture with a ratio of 6:1:1 was ball milled for 30 h and then heat treated at temperatures as high as 1000°C. The following conclusions were drawn:

(1) Nanostructured $NiTi_2$–AlNi–Al_2O_3 was produced by ball milling and subsequent heat treatment. During ball milling, both NiO and TiO_2 were reduced by Al; consequently, $NiTi_2$ was formed. The production of $NiTi_2$ was terminated after the TiO_2 had been completely consumed during ball milling.

(2) Al could reduce NiO only after the Al had melted. In the solid state, NiO was partially reduced by Al during ball milling and the heat generated by $NiTi_2$ formation enhanced NiO reduction. Al was not able to reduce TiO_2 without mechanical alloying even after the melting of Al at high temperatures.

Acknowledgement

The authors wish to thank the research board of Arak University for the financial support and the provision of the research facilities used in this work.

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