Original Research Paper

Mechanochemical synthesis of Al$_2$O$_3$/Co nanocomposite by aluminothermic reaction

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A R T I C L E   I N F O

A B S T R A C T

In this work, Al$_2$O$_3$/Co nanocomposite was successfully prepared by mechanochemical reaction between Co$_3$O$_4$ and Al powders in a planetary high energy ball mill. The mechanism of the reaction was dealt using X-ray diffraction (XRD), differential thermal analysis (DTA), and thermodynamics calculations. It was found that Co$_3$O$_4$ reacts with Al through a self-sustaining combustion reaction after an incubation period of 50 min and the reaction between Co$_3$O$_4$ and Al involves two steps. First, Co$_3$O$_4$ reacts with Al to form CoO and Al$_2$O$_3$ at the temperature around melting point of Al, and at higher temperature, CoO reacts with remaining Al to form Co and Al$_2$O$_3$. Mechanical activation process decreases the reaction temperature from 1041 °C for as-received Co$_3$O$_4$ and Al powder mixture to 869 °C for 45 min milled powders. After annealing of powder milled for 12 h, no phase transformation has been detected. The crystallite sizes of both α-Al$_2$O$_3$ and Co remained in nanometeric scale after annealing at 1000 °C for 1 h.

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1. Introduction

The alumina ceramic is one of the most widely used structural materials in modern technology for several reasons including good wear resistance and chemical stability. However, the application of alumina is limited by its high brittleness. Reinforcing of brittle ceramics by the addition of metallic or intermetallic phases is considered in modern technological processes as the possibility to obtain new materials with improved mechanical properties [1–4]. Basically, introducing the reinforcement phase can be performed by two routes. One route is ex-situ addition of reinforcement particles by techniques such as hot-pressing [5–8]. The second route is in situ formation of reinforcement phase via a displacement reaction. The later route can be done by various deposition techniques and chemical methods but mechanochemical process has some advantages over other fabrication methods such as capability of producing large quantity of materials for a low cost and nano-sized structures with high uniformity [5,9].

It is well known that when a highly exothermic chemical system is mechanically treated by ball milling, a combustion-like reaction can take place. This process is generally referred as mechanically induced self-propagating reaction (MSR). This process has the advantages of both self-propagating high-temperature synthesis (SHS) and mechanical alloying (MA) techniques [10].

Many works have been focused on synthesis of different nanocomposites e.g. Al$_2$O$_3$/Mo [4], Fe$_3$Al/Al$_2$O$_3$ [5], Zn/Al$_2$O$_3$ [11], NiTi/Al$_2$O$_3$ [12], and NiAl/Al$_2$O$_3$ [13] by mechanochemical reduction of metals oxides by Al while a few works have been done on mechanochemical reaction of Al and cobalt oxides. Li and co-workers used mechanochemical reaction between CoO and Al to prepare Co matrix with Al$_2$O$_3$ particles [9]. But synthesis of a nanocomposite with Al$_2$O$_3$ matrix and Co reinforcements via mechanochemical reaction has not been reported.

In this study, Al$_2$O$_3$/Co nanocomposite has been fabricated via redox reaction of Co$_3$O$_4$ and Al powders during milling. Also thermodynamics calculation, thermal analysis and structural evolutions were carried out to investigate the reaction mechanism.

2. Experimental procedure

The appropriate proportion of Co$_3$O$_4$ and Al powder mixture (Co$_3$O$_4$-23 wt.% Al) according to the reaction of Al and Co$_3$O$_4$ was milled in a planetary high energy ball mill using hardened chromium steel vial and balls. Ball milling was performed at room temperature under an argon atmosphere. The rotation speed of the vial and the ball to powder weight ratio were 600 rpm and 15:1, respectively. No process control agent (PCA) was used. The temperature increment of external surface of vial was recorded by a pyrometer. DTA measurements (BAHR model STA 503) were carried out to investigate the effect of milling on the Co$_3$O$_4$–Al displacement reaction. DTA experiments were conducted using Al$_2$O$_3$ crucibles, under dynamic Ar atmosphere, in the temperature range of 25–1200 °C

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and with a heating rate of 10 K min^{-1}. Annealing was performed to investigate the thermal behavior and corresponding phase transformations of milled powders. Powder samples were sealed and then annealed in a conventional tube furnace with heating rate of 10 °C min^{-1}. X-ray diffraction technique by a Philips X'PERT MPD diffractometer (Cu K$_\alpha$ radiation: λ = 0.154 nm at 20 kV and 30 mA) was used to characterize the phase composition and structural changes of the powders. The Williamson–Hall formula was used to estimate the grain size and internal strain using broadening of XRD peaks [14].

3. Results and discussions

3.1. MA and XRD analysis

Co$_3$O$_4$/Al displacement reaction in stoichiometric condition is highly exothermic and produce Al$_2$O$_3$ with 37 vol% Co:

$$3Co_3O_4 + 8Al \rightarrow 9Co + 4Al_2O_3 \quad \Delta H^\circ_{298} = -3972.8 \text{ kJ} \quad (1)$$

Fig. 1 presents the XRD patterns of powder mixture after different stages of milling. As received powder exhibited sharp crystalline peaks of aluminum and cobalt oxide (Co$_3$O$_4$). For the samples milled for >2 h all Al and Co$_3$O$_4$ diffraction peaks vanished completely and alpha alumina and cobalt peaks appeared. Both fcc and hcp crystal structures of cobalt are observed on the XRD patterns which accord with the results reported previously [3,9]. No new phase was formed for milling times shorter than 45 min therefore it can be suggested that the redox reaction occurs explosively in the period time between 45 min and 2 h. Fig. 2 shows temperature variation of the vial during milling of Co$_3$O$_4$ and Al powder mixture. The vial temperature shows an acute variation and increases from 29 to 43 °C when the powder is milled for 50 min (incubation period). A large exothermic heat release during reaction between the components can be responsible for this sudden temperature increment. Such an abrupt reaction is thought to be stimulated by a mechanism similar to SHS, which is ignited by mechanical energy from impinging balls. This result is in agreement with the XRD results and thermodynamics calculations given in the proceeding section. The pronounced broadening observed for various diffraction peaks could be related to the significant refinement of crystallite sizes of the constituting phases and increase of defect concentration as well as lattice strain induced by milling process [15]. The crystallite size of α-Al$_2$O$_3$ in the 2 h milled powder was about 35 nm which accord well with previous results in the literature [12,15]. Further milling to 12 h has appeared to have no effect on phase composition except progressive peaks broadening. The significant broadening of cobalt and α-Al$_2$O$_3$ diffraction peaks suggests that the resulting phases in final powder have nano-sized structure.
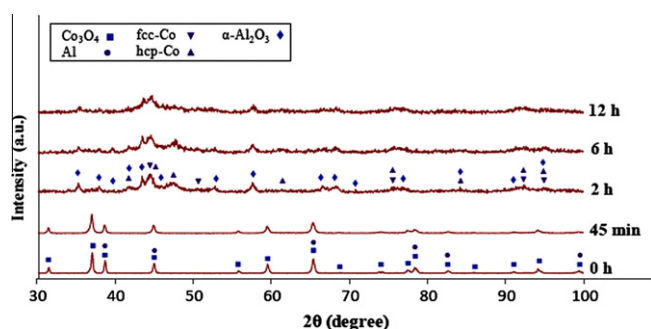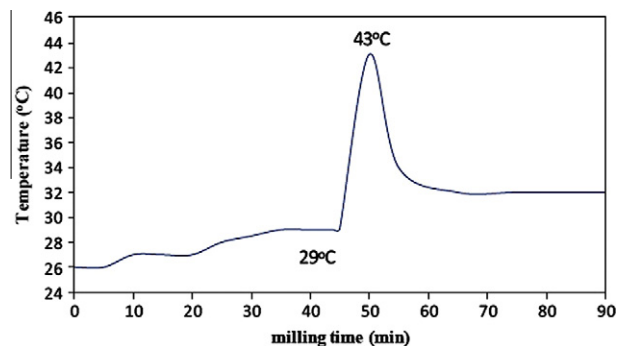

Fig. 2. Variation of vial temperature during milling process.

3.2. Thermodynamics calculations

The key to determining whether the reaction proceeds in a diffusion-controlled manner or in an unstable combustion manner is the determination of the adiabatic temperature (T_{ad}). When the reaction is exothermic enough to provide a sufficiently great adiabatic temperature, reaction can take place in self-propagating high-temperature synthesis (SHS) mode. The critical T_{ad} for propagation of a SHS reaction is about 1800 K but this minimum T_{ad} is reduced to approximately 1300 K by mechanical activation process using ball milling [16,17]. The theoretical T_{ad} associated with the redox reaction (1) can be calculated from the following equation [12,16,18].

$$-\Delta H^\circ_r = \sum \left[n^i_p \int_{298}^{T^i_m} C^i_{ps} dT \right] + \sum \left(n^i_p \Delta H^i_m \right)$$
$$+ \sum \left[n^i_p \int_{T^i_m}^{T^i_{ad}} C^i_{pl} dT \right] \quad (2)$$

Where ΔH°_r is the standard enthalpy change of the reaction, n^i_p is the molar fraction of product i, T^i_m is the melting point of product i, C^i_{ps} and C^i_{pl} are the heat capacity of product i in the solid and liquid state, respectively, and ΔH^i_m is the enthalpy of fusion of product i. The second and third terms were included in Eq. (2) when melting of the product phases occurred. If vaporizing of product i occurs too, heat capacity of product i in the vapor state (C^i_{pv}) and enthalpy of vaporization of product i (ΔH^i_v) should be included in Eq. (2) [12,16,18].

The thermodynamics data of Co$_3$O$_4$, Co and Al$_2$O$_3$ required for calculating T_{ad} are listed in Tables 1 and 2 [19]. The adiabatic temperature for redox reactions between Co$_3$O$_4$ and Al according to Eq. (2) was calculated to be 3753.3 K, which is much larger than the critical values of 1300 K and also 1800 K. Therefore it is expected that this system will react in a SHS manner.

3.3. Thermal behavior

Fig. 3 displays DTA trace of as-received Co$_3$O$_4$ and Al powder mixture. There is one exothermic and two endothermic peaks on DTA trace. The first endothermic peak at ~656 °C is due to the melting of Al (T^{Al}_m = 661 °C) [19]. The second endothermic peak at

Fig. 1. The XRD patterns of Co$_3$O$_4$–Al powder mixture milled for different times.

Table 1
Standard formation enthalpy of Al$_2$O$_3$ and Co$_3$O$_4$ [4].

Substance	ΔH°_{298} (kJ/mol)
Co$_3$O$_4$	−910
Al$_2$O$_3$	−1675.7