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Journal of Alloys and Compounds



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Mechanochemically synthesized Al₂O₃-TiC nanocomposite

E. Mohammad Sharifi*, F. Karimzadeh, M.H. Enayati

Department of Materials Engineering, Nanotechnology and Advanced Materials Institute, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Article history: Received 11 August 2009 Accepted 23 October 2009 Available online 29 October 2009

Keywords: Nanostructured materials Ceramics Mechanochemical processing

ABSTRACT

Al₂O₃-TiC nanocomposite was synthesized by ball milling of aluminum, titanium oxide and graphite powder mixtures. Effect of the milling time and heat treatment temperatures were investigated. The structural evolution of powder particles after different milling times was studied by X-ray diffractometry and scanning electron microscopy. The results showed that after 40 h of ball milling the Al/TiO₂/C reacted with a self-propagating combustion mode producing Al₂O₃-TiC nanocomposite. In final stage of milling, alumina and titanium carbide crystallite sizes were less than 10 nm. After annealing at 900 °C for 1 h, Al₂O₃ and TiC crystallite sizes remained constant, however increasing annealing temperature to 1200 °C increased Al₂O₃ and TiC crystallite size to 65 and 30 nm, respectively. No phase change was observed after annealing of the synthesized Al₂O₃-TiC powder.

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1. Introduction

 Al_2O_3 -based ceramic matrix composites are widely used in many applications, especially as excellent cutting tools [1]. Studies have shown that the addition of TiC phase to alumina matrix can improve toughness, hardness and also thermal shock resistance at temperatures up to 800 °C [2].

Al₂O₃-TiC composite is often manufactured by hot pressing of Al₂O₃ and TiC powder mixture [3,4]. However, inhomogeneous blend of starting powders, grain coarsening during sintering and weak interfaces between the ceramic particles deteriorate mechanical properties of Al₂O₃-TiC composite fabricated by this method. One possible route for introducing hard particles in the matrix of composites is the mechanochemical processing [5]. Mechanochemical synthesis involves mechanical activation of solid-state displacement reactions in a ball mill. Thus, mechanical energy is used to induce chemical reactions. The chemical precursors are typically consisted of mixtures of oxides, chlorides and/or metals that react either during milling or during subsequent heat treatment to form a composite powder [6,7]. This technique can lead to in situ formation of interpenetrating phase composites with nanosized microstructures. An important characteristic of such phases is that they exhibit properties and performance much improved over their conventional microcrystalline counterparts [8].

In this work, in situ formation of Al₂O₃–TiC nanocomposite was investigated by utilizing mechanochemical process starting from titanium oxide, aluminum and graphite powder mixtures.

The structural evolution during mechanochemical process was studied.

2. Experimental

 TiO_2 (99% purity, rutile), Al (99.5% purity, gas atomized) and graphite (99.9% purity) were mixed to produce, according to reaction (1), Al_2O_3-based nanocomposite containing 45 vol.% TiC.

$$4AI + 3TiO_2 + 3C = 2AI_2O_3 + 3TiC$$

$$\tag{1}$$

 $\Delta G^{\circ}_{298} = -1035 \text{ kJ/mol}, \Delta H^{\circ}_{298} = -1072.3 \text{ kJ/mol}$

The negative value of ΔG°_{298} suggests that reaction (1) is thermodynamically favorable at room temperature. ΔH°_{298} value is also negative, indicating that this reaction is exothermic.

Ball milling of powder mixture was carried out in a planetary ball mill at room temperature and under argon atmosphere. The ball milling media were hardened chromium steel vial (150 ml) with five hardened carbon steel balls (20 mm). The ball-to-powder weight ratio and the rotational speed of vial were 10:1 and 500 rpm, respectively. The milling was interrupted at selected times and a small amount of powder was removed for further characterizations. Phase transformation and average crystallite size were evaluated during milling by X-ray diffractometry (XRD) in a Philips X' PERT MPD diffractometer using filtered Cu K α radiation (λ = 0.15406 nm). The morphology of milled powder particles was examined by scanning electron microscopy (SEM) in a Philips XL30 at an accelerating voltage of 30 kV. Crystallite size and internal strain of specimens were calculated from broadening of XRD peaks using the Williamson–Hall method [9].

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

where θ is the Bragg's 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 $\beta \cos \theta$ versus $\sin \theta$, while the average crystallite size can be estimated from the intersect of this line at $\sin \theta = 0$.

Prepared Al_2O_3 -TiC nanocomposite powder was isothermally annealed to study the thermal behavior of as-milled powders. Powder samples were placed inside capsules and then annealed at 900 and 1200 °C for 1 h under flowing argon atmosphere

^{*} Corresponding author. Tel.: +98 312 5201676; fax: +98 311 3912752. *E-mail address:* e.mohamadsharifi@ma.iut.ac.ir (E. Mohammad Sharifi).

^{0925-8388/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2009 Published by Elsevier B.V. doi:10.1016/j.jallcom.2009.10.206



Fig. 1. XRD patterns taken from the Al/TiO $_2$ /C powder mixture after different milling times.

in a conventional tube furnace. After annealing the capsules were cooled in air. The structural evolutions occurred during annealing were determined by XRD.

3. Results and discussion

3.1. Phase evolution and reaction mechanism

 Al_2O_3 -TiC nanocomposite was synthesized according to reaction (1) which involves two reactions: reduction of TiO₂ by Al to form elemental Ti followed by the reaction of Ti with C to form TiC. These two reactions can be represented as a thermite reaction, reaction (2), and a subsequent synthesis reaction, reaction (3):

$$4AI + 3TiO_2 = 2AI_2O_3 + 3Ti,$$
 (2)

 $\Delta G^{\circ}_{298} = -500.2 \text{ kJ/mol}, \Delta H^{\circ}_{298} = -521.2 \text{ kJ/mol}$

$$Ti + C = TiC, (3)$$





Fig. 3. The XRD patterns of Al_2O_3 -TiC powder (a) as-milled for 60 h; (b) and (c) after subsequent annealing at 900 and 1200 °C for 1 h.

During ball milling in room temperature reactions (2) and (3) are thermodynamically favorable due to their negative ΔG°_{298} . The occurrence of the reaction at ambient temperatures can be however hindered by kinetic barriers. It is now well known that mechanochemical processing can provide the means to overcome the kinetics limitations of the displacement reactions [8].

Fig. 1 shows the XRD patterns of powder mixture as-received and after different milling times. The diffraction pattern of initial powder mixture shows all expected peaks of Al, TiO₂ (rutile) and graphite. With increasing milling time to 10 h, the (002) reflection of graphite disappeared indicating that graphite particles were heavily deformed and fractured into fine slices [10] and randomly mixed with Al and TiO₂ powders. In addition with increasing milling time, the intensity of Al and TiO₂ peaks decreased and their width increased as a result of refinement of crystallite size and enhancement of lattice strain.

The variation of crystallite size and lattice strain of the Al and TiO_2 powders as a function of milling time, is presented in Fig. 2. Both Al and TiO_2 powders achieved a saturated crystallite size of about 35 nm after 20 h of milling time. As expected the lattice strain of Al and TiO_2 was increased during milling time as result of increasing number of lattice defects. Refinement of the crystallite size to nanometer range and increasing the defect densities can promote the reaction kinetics by providing short-circuit diffusion paths [8].

XRD patterns after 40 h showed no crystalline TiO₂ and Al peaks. Meanwhile several additional peaks corresponding to α -Al₂O₃ and TiC compounds developed on XRD patterns. The crystallite size of α -Al₂O₃ and TiC phases after 60 h of milling time were calculated to be about 10 nm.



Fig. 2. Variation of (a) crystallite size and (b) lattice strain of Al and TiO₂ phases with milling time.



Fig. 4. SEM micrographs of as-received elemental powder particles: (a) Al, (b) TiO₂ and (c) graphite.

It was noticed that after 40 h of milling time the outside temperature of vial, measured by pyrometer, increased rapidly to 72 °C suggesting that a combustion reaction occurred between Al and TiO₂. The mechanochemical reactions generally fall into two categories, namely (a) those which occur during the mechanical activation process and there the reaction enthalpy is highly negative and (b) those which occur during subsequent thermal treatment and here the reaction enthalpy is only moderate. The first type of reaction takes place in two distinct modes, i.e., either self-propagating combustion reaction or a progressive reaction [8,11,12].

It has been suggested that the value of adiabatic temperature (T_{ad}), which is the maximum temperature achieved under adiabatic conditions as a consequence of the evolution of heat from the reaction, should be above 1800 K to yield self-propagating combustion reaction in a thermally ignited system [13]. However, the minimum T_{ad} required for the occurrence of self-propagating combustion reaction during ball milling can be significantly reduced [14,15]. This reduction in T_{ad} by mechanical activation implies that those reactions with $T_{ad} < 1800$ K can also take place with self-propagating combustion mode by mechanical activation process.

The value of T_{ad} can be calculated using following relation:

$$Q = (-\Delta H^{\circ}_{298}) = \int_{298}^{T_{ad}} \sum C_p(Products) dT$$
(4)

where Q is the heat of reaction, ΔH°_{298} is the enthalpy change at 298 K (room temperature) and C_p the heat capacities of products.

The T_{ad} for reaction (1) calculated using relation (4) and thermodynamic data [16] was found to be 2547 K which is much higher than the critical value of 1800 K. Consequently, during milling of Al/TiO₂/C mixture, reaction (1) takes place in self-propagating combustion mode. Reaction (1) can be further promoted by the dynamically maintained high reaction interface areas, as well as the short-circuit diffusion path provided by the large number of defects such as dislocations and grain boundaries induced during ball milling.

Combustion type reactions require a critical mechanical energy to be initiated. This means that a reaction which is highly exothermic can only take place after a certain time of milling [5,14]. As mentioned earlier as milling time was increased to about 40 h, reaction (2) occurred. The heat released from exothermic reaction (2) provides the activation energy for TiC formation according to reaction (3).

3.2. Thermal stability

Nanocrystalline structures are thermodynamically metastable because of the large excess free energy stored in their grain boundaries. Significant grain growth was observed in several nanocrystalline materials [17,18]. The study of thermal behavior of nanostructured materials is therefore important with respect to their possible applications.

Thermal stability of Al_2O_3 -TiC nanocomposite structure was investigated by annealing of ball-milled powders at 900 and 1200 °C for 1 h. The XRD patterns of samples as-milled for 60 h and after subsequent annealing are shown in Fig. 3. Annealing at 900 °C caused only a slight narrowing of XRD peaks indicating that no significant crystallite growth occurred at 900 °C. In contrast after annealing at 1200 °C the XRD peaks of Al_2O_3 and TiC phases were completely separated due to the crystallite growth and consequent width reduction of crystalline peaks. Nevertheless Al_2O_3 and TiC crystallite size remained in nanometer range, 65 and 30 nm, respectively even after annealing at high temperature of



Fig. 5. SEM micrographs of Al_2O_3 -TiC powder particles after (a) 5 h, (b) 20 h, (c and d) 40 h and (e) 60 h of milling times.

1200 °C. No additional change in phase composition occurred in powder particles after annealing.

3.3. Morphological changes

Fig. 4 shows the morphology of as-received Al, TiO_2 and graphite powder particles. The aluminum powder particles were irregular in shape with a size distribution of 20–100 μ m. TiO_2 powders with spherical morphology and mean particle size of 0.2 μ m show a tendency to agglomeration. The graphite particles were angular and flaky in shape with a mean particle size of 30 μ m.

Fig. 5 shows morphology of powder particles after different milling times. The plastic deformation, flattening and cold welding of aluminum powders occur in the early stage of ball milling.

After 5 h of milling time the aluminum powder particles are extensively flattened (Fig. 5a). In mean while, TiO_2 and graphite powder particles are dispersed between the Al layers. By increasing milling time to 20 h, because of work hardening of Al powder, the rate of fracturing increased and as a result the size of powder particles decreased. At this stage, the morphology of powder particles was almost equiaxed with a wide size distribution of $1-20 \,\mu\text{m}$ (Fig. 5b). The morphology of powder particles after combustion reaction, 40 h of milling time, are shown in Fig. 5c and d. Powder particles adhere together and are agglomerated due to the heat released by the combustion reaction. Further milling up to 60 h led to a significant decrease in powder particle size because of fragmentation of the brittle constituent phases, Al_2O_3 and TiC (Fig. 5e). The average powder particle size after 60 h of milling time was about 1 μ m.

4. Conclusions

Mechanochemical behavior of Al/TiO₂/C powder mixture was studied during high energy ball milling. Ball milling first only led to the broadening of Bragg's peaks as a result of reduction of the crystallite size as well as microstrain induced in the powder particles. On future milling however the Al/TiO₂/C reaction occurred with a combustion mode producing Al₂O₃-TiC structure. The Al/TiO₂/C reaction mode accords well with that predicted by corresponding T_{ad} value. It was found that Al₂O₃ and TiC phase had a nanocrystalline structure. No significant grain growth or phase change observed after annealing of ball-milled Al₂O₃-TiC powder at 1200 °C for 1 h.

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