EFFECT OF CUP AND BALL TYPES ON MECHANO-CHEMICAL SYNTHESIS OF Al_2O_3–TiC NANOCOMPOSITE POWDER

#M. ZAKERI, M.R. RAHIMIPOUR

Ceramic Department, Materials and Energy Research Center, P.O. Box: 31787/316, Karaj, Iran

#E-mail: M_zakeri@merc.ac.ir

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Al_2O_3–TiC nanocomposite powder was successfully synthesized by ball milling TiO_2, Al and graphite powders. Effects of cup and ball type, milling time and annealing were investigated. XRD was used to characterize milled and annealed powders. The morphological and microstructural evolutions were studied by SEM and TEM. Results showed that the formation of this composite begins after 20 h and completes after 35 h of milling with stainless steel cup and balls. In contrast, there is no reaction during milling (up to 80 h) with ZrO_2 cup and balls. Fe and ZrO_2 were the major impurities introduced during milling with stainless steel and ZrO_2 cups, respectively. The Fe impurity was removed by leaching in $3HCl{\cdot}HNO_3$ solution for 4 days. Mean grain size less than 7 nm was achieved at the end of milling. In spite of grain growth, this composite maintained its nanocrystalline nature after annealing at 1000°C.

INTRODUCTION

Ceramics such as Al_2O_3 have intrinsic characteristics like high melting point, high hardness, good chemical inertness and high wear resistance that make them promising candidates for high temperature structural and wear resistance components. Nowadays Al_2O_3 is widely used in cutting tools, drawing or extrusion, seal rings, valve seats, bearing parts and a variety of high temperature engine parts [1,2]. However, the use of single phase Al_2O_3 with full density in wear or structural applications is limited by the variability of their mechanical strength and their poor fracture toughness. Considerable improvement in mechanical properties of this material has been achieved by incorporating one or more other components into the base material to form ceramic-matrix composites [3, 4]. Preparation in nanostructure is another approach to improve mechanical properties [5].

There are several methods for the preparation of Al_2O_3–TiC composites [6-9] but nanocomposites of this material can be obtained easily by direct mixing of nano Al_2O_3 and TiC. But the resulting heterogeneous microstructure and high cost of the starting materials are two important drawbacks of this method. Alternatively, nanometric Al_2O_3–TiC powders can be obtained through high-energy reactive milling of mixtures of TiO_2, Al and graphite powders. The formation of alloys via solid-state reaction that occurs during ball milling, called mechanical alloying (MA), is a promising way of producing such composites. During MA both matrix and reinforcement are formed through in situ process, which will promote good bonding between matrix and reinforcement. Moreover, a homogeneous distribution of fine reinforcing particles can be obtained by the MA process [10-13].

There have been some attempts to produce Al_2O_3–TiC nanocomposite by MA. Jiang et al. investigated the in situ synthesis of Al_2O_3–TiC nanocomposite from a mixture of Ti, graphite and Al_2O_3 nanopowders by ball milling [14]. Razavi et al. used elemental powders of Ti, Al and graphite. TiC–Al_2O_3 was formed during the annealing of milled powder at oxygen atmosphere with some impurities [15]. In our previous work, Al_2O_3–TiC nanocomposites were synthesized by mechanical alloying TiO_2, Al and graphite powder mixtures [16].

Cup and balls have important effects on the phase transformation and impurity of this composite. The aim of this work is to investigate the effect of this parameter as well as milling time. For the first time, inexpensive raw materials (TiO_2, Al and graphite) were used for the preparation of this composite.

EXPERIMENTAL

The MA experiments were performed in a planetary ball mill at nominal room temperature with a vial rotation speed of 500 rpm. Pure Al (Fluka Co, 99.9%, 200 μm),

graphite (MERCK, 99.9%, 50 μm) and TiO_2 (Merck, 99.9 wt.%, 50 μm) powders were mixed according to the stoichiometry of following reaction:

$$3TiO_2 + 4Al + 3C \rightarrow 2Al_2O_3 + 3TiC \quad (1)$$
$$\Delta G^\circ_{298} = -1041 \text{ kJ}$$

Two kinds of cup and balls (stainless steel and ZrO_2) were separately used in this study. The ball to powder weight ratio (BPR) was 10:1. The mixture of the powders and balls was charged into the both of the vial (250 ml) in argon atmosphere. For preventing excess agglomeration some process controlling agent (PCA) was used (1 wt.% stearic acid). Samples for analysis were removed by interrupting the milling process at various intervals. Heat treatment of the as-milled powders was performed at 1000°C in a tube furnace in argon atmosphere (2 l/min). The heating rate was 10°C/min and the holding time at the maximum temperature was 2 h.

X-ray diffraction (XRD) profiles were recorded on a Philips diffractometer (30kV and 25mA) with Cu radiation (λ = 0.15404 nm). The recorded XRD patterns were used for the calculation of crystallite size. Prior to calculations from the XRD peaks, the background was automatically removed and the radiation was stripped from the scans using the computer software X-pert High Score developed by PANalytical B. V. (Netherlands).

Structural observations of the milled powders were carried out with a Philips EM208S transmission electron microscope (TEM) operating at 100kV. The morphology and the particle size of the mechanically alloyed powders were examined by a Philips scanning electron microscope (SEM) operating at 25kV. The Fe contents of the milled powders were measured by the inductively coupled plasma (ICP) method.

RESULTS AND DISCUSSION

The mixture of TiO_2, Al, graphite and 1 wt.% stearic acid was milled with stainless steel cup and balls. Figure 1 shows the XRD patterns of the milled powders. Initial mixing of the as received powders continues up to 10 h of milling. With increasing milling time to 20 h, the intensities of the as-received powders reflections were significantly decreased. On the other hands, TiC and Al_2O_3 reflections appeared in the pattern of the 20 h milled powder. Formation of TiC and Al_2O_3 is on the basis of reaction (1) due to its negative Gibbs free energy at room temperature. This reaction progresses gradually and completes after 35 h of milling. Increasing milling time to 80 h had no change except peak broadening that is due to the microstructural refinement.

The Fe reflection appeared after 20 h and can still be seen at the end of milling. Due to the much broadening and overlapping of the reflections, it was very difficult to make a decision about the Fe reflection. For more clarification, the 80 h milled powder, was annealed at 1000°C. As seen in Figure 2, the sharp reflection of the Fe can clearly be distinguished due to the grain growth and strain release. The Fe content of the milled powders was measured by the ICP method. As seen in Table 1, the powders milled for 35 and 80 h have 18.1 and 29.9 % Fe impurity, respectively. The large difference between the hardness of synthesized phases and cup materials promotes the wearing of cup and balls during milling. Approximate values of 14.4, 30 and 7 GPa were reported for the hardness of Al_2O_3, TiC and stainless steel, respectively [17].

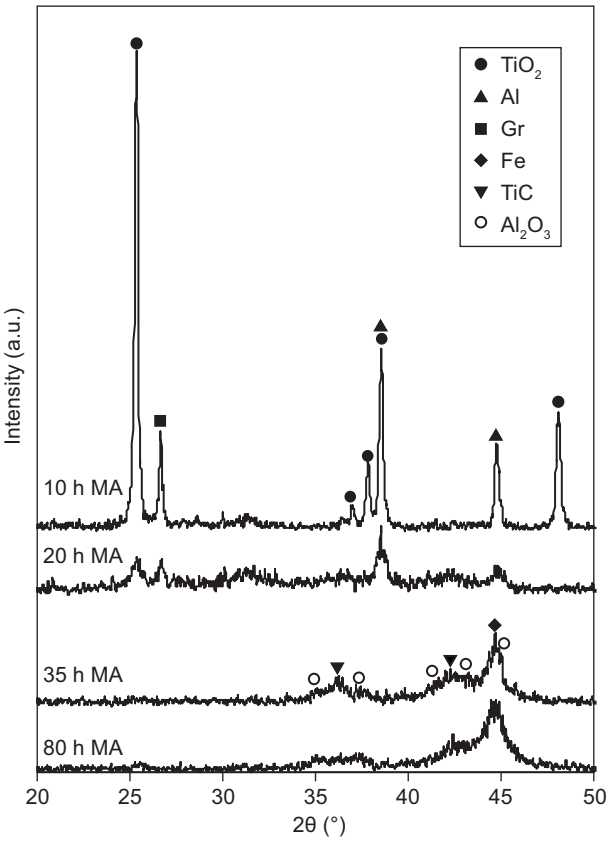


Figure 1. XRD patterns of the powders milled by stainless steel cup and balls.

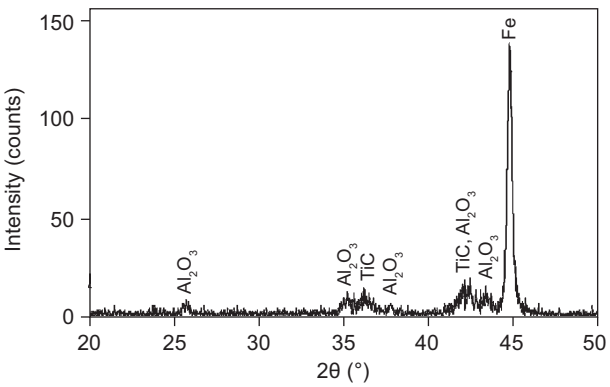


Figure 2. XRD pattern of the 80 h milled sample after annealing at 1000°C (stainless steel cup and balls).

Table 1. Effect of the milling time on the Fe content and grain size (stainless steel cup and balls).

Milling time (h)	As received	5	10	20	35	50	80	80 h, 1000°C
Fe (%)	–	–	–	–	18.08	–	29.86	–
Mean grain size (nm)	148 (TiO_2)	91 (TiO_2)	70 (TiO_2)	17 (TiO_2)	12 (Fe)	8 (Fe)	7 (Fe)	52 (Fe)

The Fe impurity must be removed from the Al_2O_3––TiC composite powder. There are two approaches for this purpose; the first one is using of a cup and ball with higher hardness and the second one is leaching of the milled powder with a strong acid. The milling experiments were repeated with ZrO_2 cup and balls at the same conditions as with stainless steel cup and balls. The XRD patterns of the milled powders at new condition are shown in

Figure 3. There is no reaction between the starting materials. TiO_2 reflections can be seen until 80 h of milling. The lower density of ZrO_2 (approx. 6.0 g.cm^{-3}) in comparison with stainless steel (7.8 g.cm^{-3}) leads to the decrease of the milling energy. For obtaining Al_2O_3-TiC composites with ZrO_2 cup and balls at shorter milling time, the energy of the ball mill must be increased by higher BPR, higher rotation speed, etc. The ZrO_2 peak appeared in the pattern of the 80 h milled sample due to the wear of the ZrO_2 cup and balls. The existence of ZrO_2 impurity in the milled powder indicates that it is impossible to synthesize Al_2O_3-TiC composite powder with ZrO_2 cup and balls because the ZrO_2 impurity can not be removed by conventional leaching methods. There is only one approach to prepare this composite without any impurity; use of cup and balls with the same composition of the products such as Al_2O_3 or TiC.

As discussed before, the Fe impurity of the milled powders can easily be removed by a conventional leaching method. The 35 h milled powder was leached by 3HCl.HNO_3 solution for 4 days. The XRD pattern of the leached powder after sieving and drying is presented in Figure 4. As seen, there is no reflection of Fe in this pattern. On the other hand, the Al_2O_3 and TiC reflections can clearly be seen. For confirmation, the Fe content of this sample was measured by the ICP method. There is only 0.3 % Fe in this sample after leaching.

The cross section of the 35 h milled powder is presented in Figure 5a using the back scattered mode of SEM. There is a distribution of light grains in this cross section. Energy dispersive spectroscopy (EDS) indicates that these grains are corresponding to Fe impurity that introduced from stainless cup and balls (Figure 5b). The cross section of the powder after leaching is shown in Figure 5c. It is evident that there is no light grain corresponding to Fe impurity. The Ti map representative of the TiC distribution is shown in Figure 5d. The distribution of Ti in this cross section is uniform that means TiC particles were homogeneously distributed in the Al_2O_3 matrix composite. Al_2O_3 and TiC grains cannot be characterized because of their nanocrystalline nature.

The mean grain size of the milled powders was measured by the well-known Scherrer method [18]. The mean grain size of TiO_2 decreases in the early stage of milling and reaches a value of 17 nm before the formation of products (Table 1). At longer milling time, it was impossible to calculate the grain size of Al_2O_3 and TiC due to much broadening and overlapping of their reflections, thus the mean grain size of Fe was calcu-

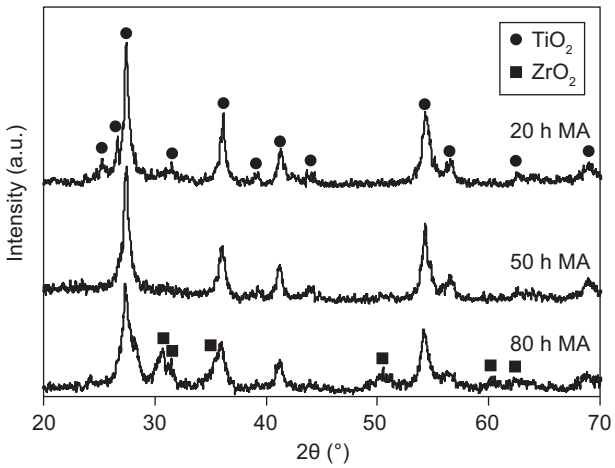


Figure 3. XRD pattern of the powders milled by ZrO_2 cup and balls.

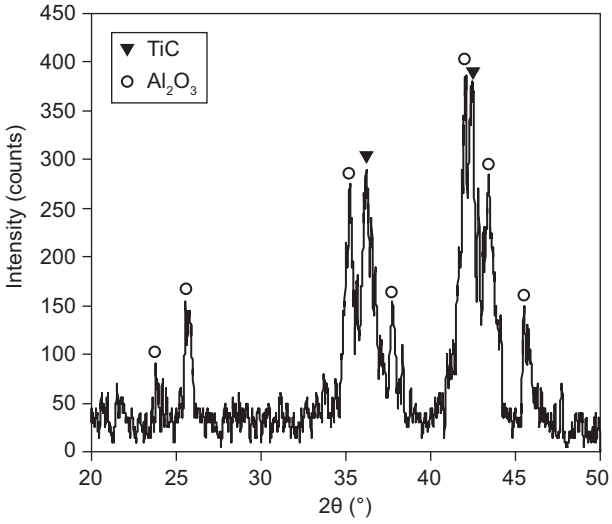


Figure 4. XRD pattern of the 35 h powder milled after leaching with 3HCl–HNO_3.

lated as the representative of composite microstructure. The materials with lower melting points have usually larger grain size due to the milling and vice versa [19]. Therefore, it can be concluded that the mean grain size of Al_2O_3 and TiC is smaller than that of Fe. It means Al_2O_3-TiC nanocomposite powder with a mean grain size less than 7 nm was obtained at the end of milling (80 h). In spite of significant grain growth, the 80 h milled powder maintained its nanocrystalline nature after annealing at 1000°C. The TEM image of the 80 h milled sample in Figure 6, confirms the XRD results.

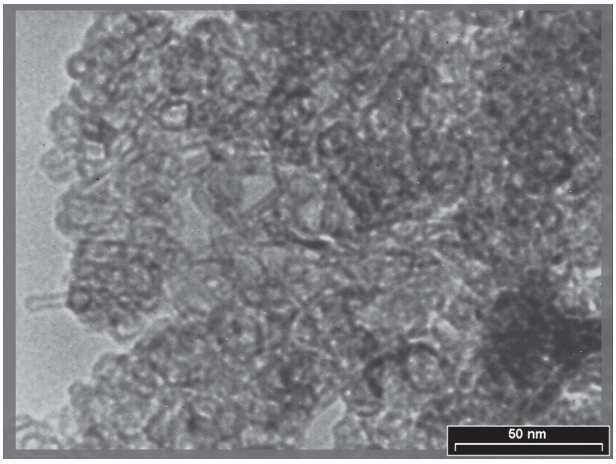
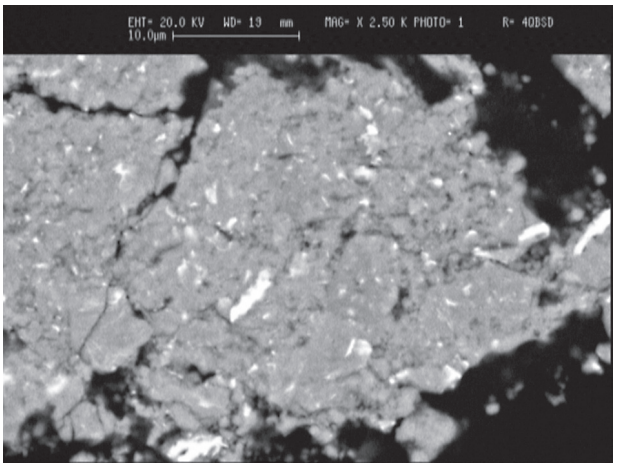


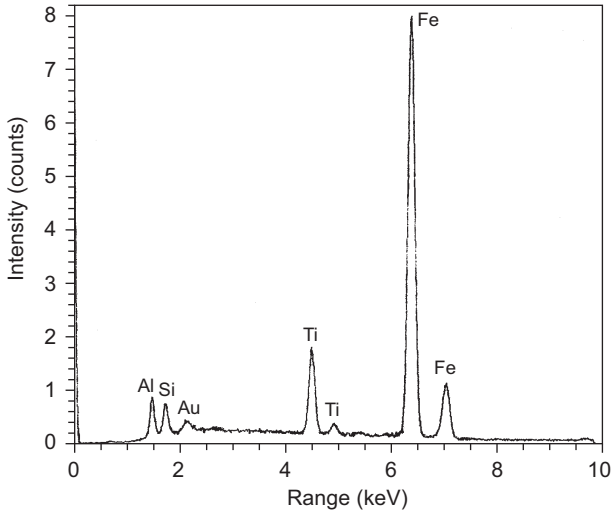
Figure 6. Bright field image of the 80 h milled sample with stainless steel cup and balls.

CONCLUSION

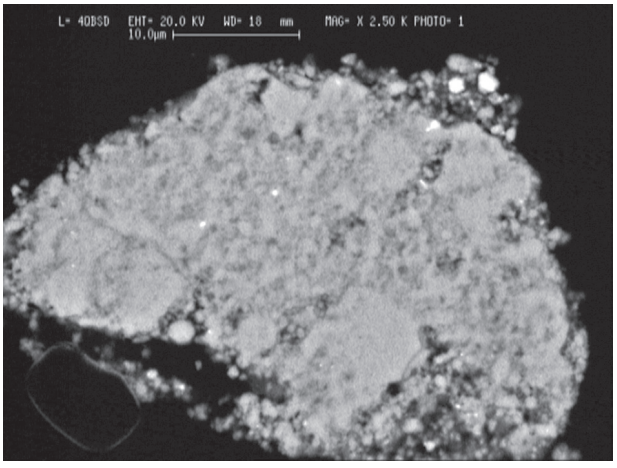
The feasibility of in situ synthesizing of Al_2O_3–TiC nanocomposite powder was investigated by ball milling of TiO_2, Al and graphite powders. Formation of this composite begins after 20 h and completes after 35 h of milling with stainless steel cup and balls.



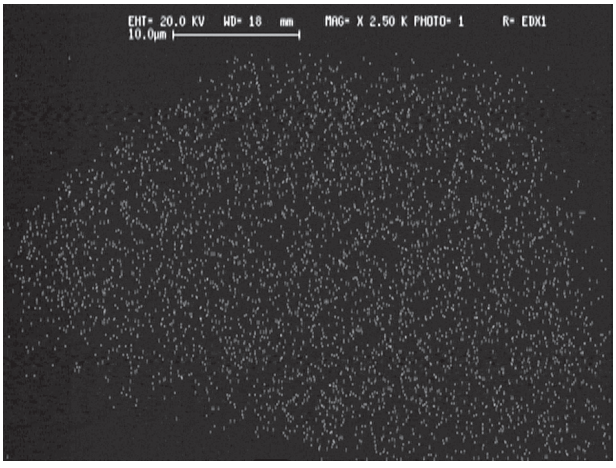
a)



b)



c)



d)

Figure 5. Back scattered images of the 35 h milled powders a) before leaching, b) EDS analysis of the marked grain, c) after leaching and d) Ti map of image c).

On the other hand, there is no reaction during milling with ZrO_2 cup and balls. Fe and ZrO_2 were the major impurities introduced during milling with stainless steel and ZrO_2 cups, respectively. The Fe impurity was removed by leaching in $3HCl{\cdot}HNO_3$ solution for 4 days. A homogeneous distribution of Al_2O_3 and TiC was obtained on the basis of back scattered of SEM images. A mean grain size less than 7 nm was obtained at the end of milling according to the Scherrer formula which is in agreement with TEM images. In spite of grain growth, this composite maintained its nanocrystalline nature after annealing at 1000°C.

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