Effect of Fabrication Method on Microstructure and Properties of Al$_2$O$_3$–TiC Composites

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Al$_2$O$_3$–TiC composite powders were prepared by high-energy ball milling (HEBM) and wet-planetary ball milling (WPBM) from different starting materials, and subsequently sintered by Spark Plasma Sintering (SPS). The effect of the fabrication method on the microstructure and properties of Al$_2$O$_3$–TiC composites was investigated. The results showed that Al$_2$O$_3$–TiC composites with fine and homogeneous microstructures were prepared by SPS from high-energy ball milled reactants, which had excellent comprehensive properties: bending strength of 944 ± 21 MPa, Vickers hardness of 21.0 ± 0.3 GPa, fracture toughness of 3.87 ± 0.20 MPa·m$^{1/2}$, and electrical conductivity of $1.2787 \times 10^5$ S·m$^{-1}$. The relationship between microstructure and properties and the strengthening and toughening mechanisms was discussed.

In comparison with the traditional WPBM route, HEBM was a favorable technique used to produce a high homogeneous microstructure and promising mechanical and electrical conduction properties.

(Received March 14, 2005; Accepted June 30, 2005; Published September 15, 2005)

Keywords: high-energy ball milling, spark plasma sintering, alumina–titanium carbide

1. Introduction

Particulate composites have been primarily prepared by sintering mechanically mixed powders of the constituent phases. During this process, the distribution and homogenization of the second-phase particles in the matrix is strongly dependent on the particle morphology (shape and size) of the starting powders and dispersing process. Another route to fabricate particulate composites is in-situ reaction synthesis, which is advantageous for producing particulate composites with finer and more homogeneous microstructures, higher chemical and microstructural stability at a high temperature, and mechanical properties better than those obtained by the conventional processes.1,2) Thus, it is suitable to be employed in in-situ synthesized fine-grained Al$_2$O$_3$–TiC composites that have wide applications such as cutting tools and substrates of magnetic heads. The in-situ synthesis route can be realized by a combination of high-energy ball milling (HEBM) and spark plasma sintering (SPS) techniques.

HEBM (reactive milling) has been used widely as a non-equilibrium mechanical processing method to synthesize nanostructured powders.3,4) During the reactive milling process, chemical reactions can occur in addition to the reduction of grain size. For example, it has been reported that Al$_2$O$_3$–TiC nanocomposite powders were successfully prepared by HEBM,5) but few studies concerning the microstructure and mechanical properties of structural ceramics produced through HEBM have been reported in literature.

The SPS technique is highly effective for producing fine-grained, fully-dense materials. The integration of fast heating and cooling rates, short processing time, and applied pressure makes this technique a powerful tool for better control of microstructure and optimization of properties.6,7) In this paper, the microstructure and properties of fine-grained Al$_2$O$_3$–TiC composites fabricated by SPS from high-energy ball milled reactants were investigated and compared with those of the composites prepared from direct mixtures of Al$_2$O$_3$ and TiC powders by SPS.

2. Experimental Procedures

The raw materials used were 99.5% pure titanium powder (−325 mesh, Shanxi Bongen Titanium Co. Ltd., Shanxi, China), 99.9% pure graphite powder (−325 mesh, Shanghai Carbon Materials Factory, Shanghai, China), 99.9% pure alumina (average particle size of 400 nm, Shanghai Wusong Chemical Factory, Shanghai, China) and 99.0% pure titanium (average particle size of 400 nm, the Mineralogical Society of Japan). Two types of Al$_2$O$_3$–TiC powder mixtures were prepared by two different methods with different starting materials: (1) In-situ reaction by HEBM: titanium and graphite powders with a molar ratio of 1 : 0.95 were mixed with Al$_2$O$_3$ powder to yield a TiC content of 40 mass% in the end product. The mixed powders were placed a steel vial along with a series of hardened steel balls further, the ball-to-powder weight ratio was 13 : 1. The steel vial was subsequently sealed under argon atmosphere. The milling was conducted using the HEBM machine (Model GN-2, Shenyang Science Equipment Factory, Shengyang, China) that had a milling speed of 480 rpm. The milling was interrupted after every 5 h for cooling. The collected powder after 25 h-HEBM was analyzed by means of an X-ray diffractometry (XRD) with CuKα radiation (Model D/max 2550V, Rigaku, Tokyo, Japan); (2) Wet milling method: Al$_2$O$_3$ and TiC powders with a weight ratio of 60 : 40 were directly mixed together with Al$_2$O$_3$ balls (the ratio of ball to powder was 4 : 1) in ethanol for 24 h by planetary ball milling, and then dried and sieved. The above mentioned powder mixtures were put into a graphite die (15 mm in diameter) and sintered using the Dr. Sinter® 2040 spark plasma sintering system (Sumitomo Coal Mining Co., Tokyo, Japan) in vacuum (less than 4 Pa). The
heating rate was around 50 K/min and the pressure was applied at the final stage of the sintering process and maintained constant (at 50 MPa). The temperature was held at 1753 K for 4 min before the power was switched off.

The surfaces of both as-sintered samples were ground to remove the graphite layers and then polished using diamond pastes with different particle sizes (ranging from 3.5 to 0.5 μm). The phase constituents of the sintered sample prepared by in-situ reaction were analyzed using XRD. The densities of consolidated specimens were obtained using the Archimedes immersion method with deionized water as the immersion medium. The theoretical densities of the specimens were calculated according to the mixture rule. The microstructure was observed using a Field Emission Scanning Electron Microscope (JSM-6700F, JEOL, Japan). The grain sizes were estimated from the SEM micrographs of fracture surfaces. The samples were machined to 1 x 1.3 x 12 mm³ bars with a span of 10 mm for the three point bending strength (σy) test. Six beams were tested for each material. Vickers hardness (HV) and fracture toughness (KIC) were measured with an indentation technique (Wilson-wolpert Tukon® 2100B). The indentation parameters were measured using 5-kg load with a dwelling time of 10 s. A half-penny shaped crack was observed after indentation. Six normal values of crack length were obtained, and subsequently, the following equation was then used to calculate the fracture toughness:

\[ K_{IC} = 0.016 (E/H_v)^{1/2} (P/c^{3/2}) \]

where \( E \), \( H_v \), \( P \) and \( c \) refer to Young’s modulus, Vickers hardness, the applied indentation load, and the half-length of the radial crack, respectively. The modulus \( E \) has been reported to increase nearly linearly with an increase in the TiC content in the range of 0 to 40 mass\%. According to this relation, as \( E(Al_2O_3) = 393 \text{ GPa} \) and \( E(TiC) = 460 \text{ GPa} \), we had \( E(Al_2O_3/40\text{mass\%TiC}) = 416 \text{ GPa} \). The electrical conductivity (σ) of sintered bodies was measured by the four-probe method. The continuity of the TiC phase in the composites was quantified in terms of the Betti number that is an index involving geometrical topology and can characterize the three-dimensional continuity of phases. Its value was determined on basis of the polished surface (the area of 12.7 x 9.6 mm²) by using an image analyzer (Image Pro Plus 4.1). When the Betti number for a particular phase equals to zero, the phase is discontinuous, on the other hand, for a Betti number larger than zero, the phase becomes continuous. Moreover an increase in the Betti number implies that the phase becomes more continuous.

3. Results and Discussion

3.1 Microstructures

Figures 1(a), (b) and (c) shows the XRD patterns of raw materials, powders mixtures in-situ synthesized by 25 h-HEBM, and the sample sintered by SPS at 1753 K for 4 min under 50 MPa following 25 h-HEBM, respectively. It could be seen in Fig. 1(b) that after 25 h-HEBM the peaks of Ti and C were hardly visible. Evidently, the disappearance of Ti and C during milling was the result of the reaction to form TiC, and this is confirmed by the existence of the TiC peaks. On the basis of the peak intensity of the reactant and resultant, it was concluded that the reaction was almost complete. The broadening of the Al₂O₃ peaks was primarily due to the refinement of the crystalline size and an increase in strain. The XRD pattern of the in-situ reacted and sintered sample [Fig. 1(c)] showed that only Al₂O₃ and TiC phases were detected, implying the completeness of the following reaction:

\[ Al_2O_3 + Ti + C \rightarrow Al_2O_3 + TiC \; (40 \text{ mass\%}) \]

The microstructural morphologies of the polished surface of the sintered samples are shown in Fig. 2. The gray-white phase is TiC and the dark phase Al₂O₃. In the case of a reactive milled material [Fig. 2(a)], fine-grained TiC particles are distributed homogeneously in the Al₂O₃ matrix. In contrast, the phase distribution of the bulk material treated by the WPBM [Fig. 2(b)] was apparently less uniform than that of the former, and there even existed some clusters or abnormally grown grains in the latter material. The relative densities of the former and latter samples, both achieving near-full density, were 99.2 and 99.3%, respectively.

SEM photographs of the fracture surface of the sintered sample are shown in Fig. 3. Figure 3(a) shows that the distribution of grain size was very narrow, while in Fig. 3(b), we observe that some grains grew to a extremely large extent in local areas. The result observed was in good agreement with that shown in Fig. 2. During the SPS process after the HEBM, the abnormal growth of grains was effectively restrained so as to accommodate the growth of TiC limited by the Al₂O₃ grains and the inter-constraint grain growth for the two-phase system. In comparison, during the SPS process after the WPBM, although the inter-constraint grain growth still existed in a long range, the grains grew abruptly in some local regions.

The grain sizes of both Al₂O₃ and TiC [in Fig. 3(a)] were less than 500 nm. According to the TEM image (not shown), their mean grain sizes of them were around 400 and 200 nm, respectively. In Fig. 3(b), the mean grain sizes of both Al₂O₃ and TiC were around 1 and 0.6 μm, respectively, larger than...
those of grains shown in Fig. 3(a). Considering the particle sizes and particle shape of starting materials, it could be concluded that the microstructure was affected to a small extent by the morphology of the starting materials for the composites prepared by HEBM, while it was affected to a larger extent in the case of the composites prepared by WPBM. Additionally, it should be noted that owing to adoptions of the advanced sintering technique in this work, even the microstructure of the Al₂O₃–TiC composites prepared by WPBM were finer than that of the commercial Al₂O₃–TiC composites fabricated by conventional sintering techniques, such as hot pressing and pressureless sintering, whose grain sizes were around 2–5 μm.

3.2 Evaluation of properties
The mechanical properties and electrical conductivity of the sintered specimens are listed in Table 1. The specimen prepared by the in-situ reaction via HEBM exhibited higher bending strength, slightly higher hardness, higher electrical conductivity and lower fracture toughness than the one prepared by WPBM. There are two reasons for the high strength of fine-grained composites. First the refinement of the Al₂O₃ matrix resulting from the highly efficient milling action and the suppression of the TiC grain growth is beneficial for the improvement of strength. Secondly, the reduction in the flaw size of composites with fine reinforcing TiC particles is accepted as an important reason for the...
increase in strength. In accordance with the theory of material mechanics, the relationship among the strength ($\sigma_b$), fracture toughness ($K_{IC}$), and critical (biggest) flaw size ($L$), that is, the depth of a surface flaw or the half-size of a body flaw, satisfies the following relationship: 13)

$$\sigma_b = \frac{Y}{L^{1/2}} K_{IC}$$

where $Y$ is a dimensionless geometrical parameter and a constant in this paper. According to eq. (3), the strength of this type of brittle ceramics is determined by the fracture toughness and critical flaw size that is very relative to the grain size of $\text{Al}_2\text{O}_3$ and TiC. Although the fracture toughness of fine-grained $\text{Al}_2\text{O}_3$–TiC composites is slightly lower than that of the coarse-grained ones in this work, the decrease in the critical flaw size may have improved the bending strength. As shown in Fig. 3 and Table 1, the grain sizes of both $\text{Al}_2\text{O}_3$ and TiC in the composites prepared by HEBM are smaller than that in the composites fabricated by the WPBM. Therefore, it can be concluded that the observed high strength of fine-grained composites is attributed mainly to the reduction in the critical flaw size resulting from microstructural refinement. Furthermore, in-situ reaction processing is advantageous for the elimination of the amorphous grain boundary film and obtaining composites with a clean interface between reinforcing particles and matrix particles. As described in Ref. 14), it raises the critical stress intensity of the fracture of the grain boundary, which results in an increase in strength. Intergranular and transgranular fractures coexisted in the particulate composites both in Fig. 3(a) and (b). It should be noted that the fracture of the $\text{Al}_2\text{O}_3$ matrix was primarily transgranular, while much of the intergranular fracture was found in the reinforcing TiC particles.

Figures 4(a) and (b) show typical patterns of Vickers indentation cracks in the polished surface of the sintered samples. The length of the radial cracks were measured and used for the calculation of fracture toughness from eq. (1). The results (listed in Table 1) showed that fine-grained materials did not exhibit a value higher value than the coarse-grained materials, as indicated in literatures.11,12,15–18) The low fracture toughness in the fine-grained $\text{Al}_2\text{O}_3$–TiC composites of this study could be attributed to the following reasons. The fracture toughness of the monolithic $\text{Al}_2\text{O}_3$ decreases with the reduction in grain size. It was reported that the $K_{IC}$ value of monolithic $\text{Al}_2\text{O}_3$ with a grain size of 350 nm was only $3.3 \pm 0.14 \text{ MPa-m}^{1/2}$.19) On the other hand, the crack bridging and crack deflection (shown in Fig. 5) that are regarded as the major toughening mechanisms in the $\text{Al}_2\text{O}_3$–TiC composites,20) are less effective in improving fracture toughness since the grain size of the toughening phase is in the near-nano scale. In comparison with the $K_{IC}$ value of monolithic $\text{Al}_2\text{O}_3$, the fracture toughness of the in-situ synthesized $\text{Al}_2\text{O}_3$–TiC composites was slightly higher: $3.87 \pm 0.20 \text{ MPa-m}^{1/2}$.

The electrical conduction for $\text{Al}_2\text{O}_3$–TiC composites is attributed to the formation of a network of electrically conductive TiC phase ($2 \times 10^6 \text{ S-m}^{-1}$) within the insulating $\text{Al}_2\text{O}_3$ phase ($2 \times 10^{-13} \text{ S-m}^{-1}$), hence, the distribution of the
TiC phase is one of the critical factors for electrical conductivity.\textsuperscript{21)} The result of the image analysis showed that the Betti numbers of the TiC phase in the fine-grained and coarse-grained composites were 23 and 10, respectively. This result indicated that the TiC phase in both the samples formed a continuous network further, the TiC phase became more continuous in the fine-grained composites. This corresponded with the fact that the electrical conductivity of fine-grained material was higher than that of coarse-grained material of the same chemical composition in Table 1. Additionally, the clean interface between \textit{in-situ} reacted TiC grains also caused an improvement in the electrical conductivity.

4. Conclusions

(1) Al\textsubscript{2}O\textsubscript{3}–TiC composites were fabricated by SPS from high energy ball milled elemental titanium, graphite, and alumina with a finer and more homogeneous microstructure than those prepared from the direct mixing of submicron Al\textsubscript{2}O\textsubscript{3} and TiC powders.

(2) The fine-grained Al\textsubscript{2}O\textsubscript{3}–TiC composites prepared by HEBM possessed superior mechanical properties and electrical conductivity as compared to the coarse-grained composites, except for a slightly lower fracture toughness.

Acknowledgments

We gratefully acknowledge the financial support provided by the Natural Science Foundation of China (Nos. 50302012 and 50232020) and the Open Foundation of State Key Laboratory (No. SKL:200504SIC).

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