Fabrication of SiC-TiC Composites via Mechanochemical Synthesis

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ABSTRACT

SiC-TiC composites have been fabricated by using a mechanochemical processing of a mixture of Si, Ti, and C at room temperature and subsequent hot-pressing. TiC powders have been obtained by the mechanochemical processing of a mixture of Ti and C whereas SiC powders has not been obtained from a mixture of Si and C. By using the exothermic reaction between Ti and C, SiC-TiC powder could be obtained from the mixture of Si, Ti, and C using the mechanochemical processing for more than 12 h. The X-ray diffraction analysis has shown that the powder subjected to the mechanochemical processing consisted of the particles having crystallite size below 10 nm. Fully densified SiC-TiC composites have been obtained by hot-pressing of the powder at 1850 °C for 3 h and it has shown comparable mechanical properties to those of the SiC-TiC composites prepared from the commercially available SiC and TiC powders. Flexural strength of 560 MPa and fracture toughness of 4.8 MP $\cdot$ am$^{1/2}$ have been shown for the SiC-TiC composites with composition corresponding to 0.75 : 0.25 : 1 mole ratio of Si : Ti : C.

Key words : Mechanochemical process, SiC, TiC, Composites

I. Introduction

Because of excellent mechanical properties at room- and high temperature, and high wear- and good thermal resistance, SiC is the suitable materials for high temperature structural applications. SiC, however, has limitations to actual usage for its low fracture toughness. To improve the fracture toughness, SiC-TiC composites have been studied.[1-5] It has been shown that SiC-TiC composites have the superior fracture toughness compared to monolithic SiC. The crack deflection at the front of TiC particles caused by residual thermal stress between SiC and TiC particles mainly contributes to the superior fracture toughness.[1-5] Since the brittle-ductile transition in TiC occurs at around 800°C, toughening due to plastic deformation can also be expected in SiC-TiC composites at high temperature.[6] Furthermore, SiC-TiC composites can be machined by the electrical discharge machining (EMD) method due to the low electrical resistance of TiC ($5.3 \times 10^{-5} \Omega \cdot$ cm). EMD is one of the candidate methods to save the machining cost that hinder the application of SiC ceramics.

Recently, mechanochemical synthesis (McS) has been investigated for obtaining ceramics powders such as ZrO_2, $Pb(Mg_{1/3}Nb_{2/3})O_3$, and $TiN-Al_2O_3$ composites.[7-10] The process utilizes the activation energy of solid-state reaction by mechanical energy instead of thermal energy and has several advantages over both conventional solid-state reaction and wet-chemical process including using low-cost raw materials, simplicity of the process, and obtaining fine par-

ticles. It is interesting that the powders obtained by McS usually have a crystallite size of nano meters and highly disordered crystal structure,[7-10] which could act as a strong densification driving force. Therefore, McS can be considered as the process for preparing powders of covalent bonded materials (e.g., SiC) for easy densification.

SiC is one of the materials difficult to be synthesized by McS due to the positive heat of reaction for the formation of SiC. On the other hand, TiC has been readily synthesized from a mixture of Ti and carbon by McS due to the negative heat of reaction.[11-12] It has also been reported that the one reaction having negative heat of reaction can contribute to proceeding of the other reactions.[13-14] Therefore, although preparation of SiC by McS is difficult, SiC-TiC powders could be readily prepared by McS. In this study, SiC-TiC powders were prepared from a mixture of Si, Ti, and C by McS. Dense SiC-TiC composites were prepared by hot-pressing of the SiC-TiC powders, the properties of composites were characterized and compared to those of the SiC-TiC composite prepared from commercially available SiC and TiC powders.

2. Experimental

Si (99.9%, Alfa, USA), Ti (99.98%, Aldrich, USA) and C (graphite 99.9%, Alfa, USA) powders were used as starting materials. Three powder mixtures were prepared with compositions corresponding to 0.9 : 0.1 : 1, 0.75 : 0.25 : 1, and 0.5 : 0.5 : 1 of the mole ratio of Si : Ti : C, respectively, to prepare SiC-TiC powders. Ten grams of the mixtures was loaded into a cylindrical hardened steel vial together with the stainless steel balls 12.7 mm in diameter. McS was con-

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ducted in a shaker mill (Model 8000, Spex Industries, Edison, NJ, USA) for 24 h in air. For comparison, McS of a mixture of Si and C (mole ratio 1 : 1) and a mixture of Ti and C (mole ratio 1 : 1) was also conducted. Our previous studies[10,15] indicate that Fe with amount of < 1 w/o is contaminated in the synthesized $LiMn_2O_4$ or TiB_2 powders by McS for 24 h. Therefore, contamination of a little Fe (~1 w/o) is expected in the powders obtained in this study. The contamination of oxygen is neglected in this study since it could be removed by the reaction with carbon during McS. The residual carbon is also neglected since it has not been observed in the X-ray diffractometry (XRD) analysis. SiC-TiC composites were prepared by hot-pressing of the SiC-TiC powders, which were obtained via McS, with 4 wt% Y_2O_3-2 wt% Al_2O_3 as sintering additives at 1850°C for 3 h under 25 MPa in an Ar atmosphere. The phases of the powders and composites were determined by XRD. The crystalline sizes of the powders were determined by the Debye-Scherrer equation. The microstructure of composites was observed by scanning electron microscopy (SEM). Flexural strength and fracture toughness of the composites were characterized by four-point bending tests with 2 mm × 1.5 mm × 25 mm bars and the indentation-strength method, respectively.

3. Results and Discussion

Fig. 1 (a) shows the XRD results of the powders prepared by McS of the mixture of Ti and C. The peaks of Ti and C have been observed for the powders subjected to 1 and 2 h of McS, however, the sharp peaks of TiC phase have been observed for the powders subjected to 3 h of McS. It indicates that the solid-state reactions between Ti and C have occurred during McS. It is interesting that the formation of compound (i.e., TiC) in the mixture of Ti and C during McS shows two different aspects as compared to McS of the other covalent-bonded and ionic-bonded materials (e.g., $LiMn_2O_4$[10] and TiB_2[15]). First, TiC has been formed in the early stage of McS as compared to TiB_2 or $LiMn_2O_4$, which have been formed after 24 h of McS. Second, the sharp and strong peaks of TiC have been observed at first and then it has gradually broadened and weakened with McS. On the other hand, the sharp and strong peaks have not been observed in McS of other materials including TiB_2 and $LiMn_2O_4$.[8-10,15] It is believed that the negative heat of reaction for the formation for TiC is responsible to the different synthesis behavior of TiC. The heat of reaction for TiC is -108 kJ/mole at room temperature (around 298K), which is a higher value as compared to that of the other materials, and it may contribute to the formation of well developed-, and large sized TiC crystalline in the early stage of McS. In other words, both the thermal and mechanical energy contribute to the formation of TiC in the early stage of McS. The refinement of crystalline size and the introduction of internal strain have subsequently occurred due to the application of extensive mechanical energy to the powders and,
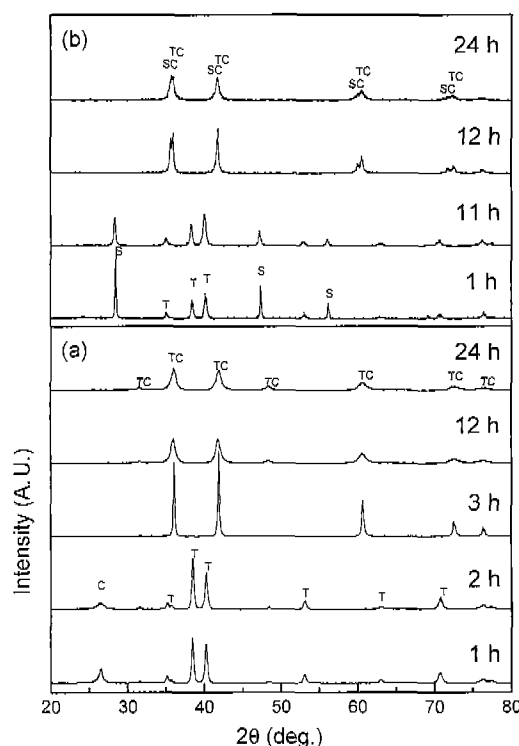

Fig. 1. XRD patterns of the mixture of (a) Ti and C, and (b) Si, Ti, and C (0.5 : 0.5 : 1 of mole ratio) subjected to mechanochemical process as a function of time.

consequently, the diffraction peaks have been broadened and decreased with McS. On the other hand, the thermal energy could not play an important role on the formation of $LiMn_2O_4$, TiB_2 and other compounds having the small value of heat of reaction. Therefore, broad and weak peaks of the compounds are appeared at the beginning of McS for these materials that reflects the primary role of mechanicanical energy for the formation of compounds.

The broad peaks of TiC shown in Fig. 1 (a) implies that the powder subjected to over 12 h of McS has a very small crystallite size and/or some degree of amorphous state, which are frequently observed in the powders subjected to McS.[7-10,15] In Fig. 1 (a), the peaks corresponded to graphite have been decreased rapidly due to its lower absorption effects and fracture.[11-12]

SiC has not been obtained by McS of the mixture of Si and C. It is due to the positive heat of reaction between Si and C that hinder the formation of SiC. It means that the mechanical energy applied to the powders during McS is not enough to overcome the activation energy of the reaction between Si and C.

Fig. 1 (b) shows the XRD results of powders prepared by McS of the mixture of Si, Ti, and C (mole ratio of 0.5 : 0.5 : 1). It shows the formation of SiC-TiC phases in the powders subjected to over 12 h of McS. As compared to McS of the mixture of Ti and C, Fig. 1(b) shows that the formation of TiC takes longer time. It may be due to the less amount of Ti in the mixtures and consume the heat of reaction from
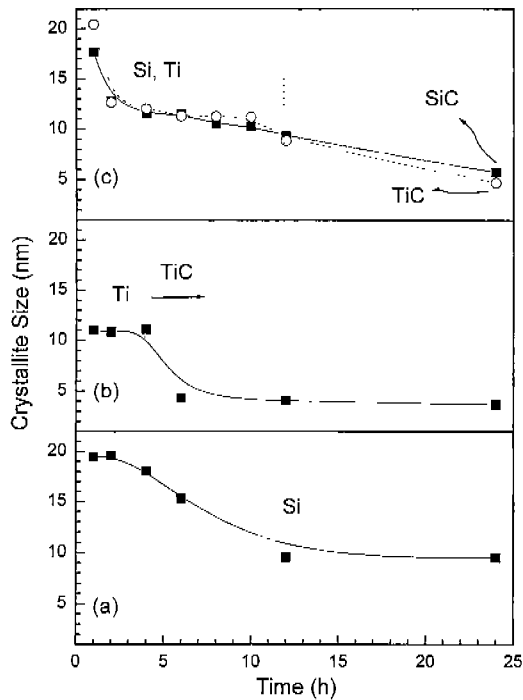
Fig. 2. Variations of crystallite size of (a) Si in the mixture of Si and C, (b) TiC in the mixture of Ti and C, and (c) SiC and TiC in the mixture of Si, Ti and C subjected to mechanochemical process as a function of time.
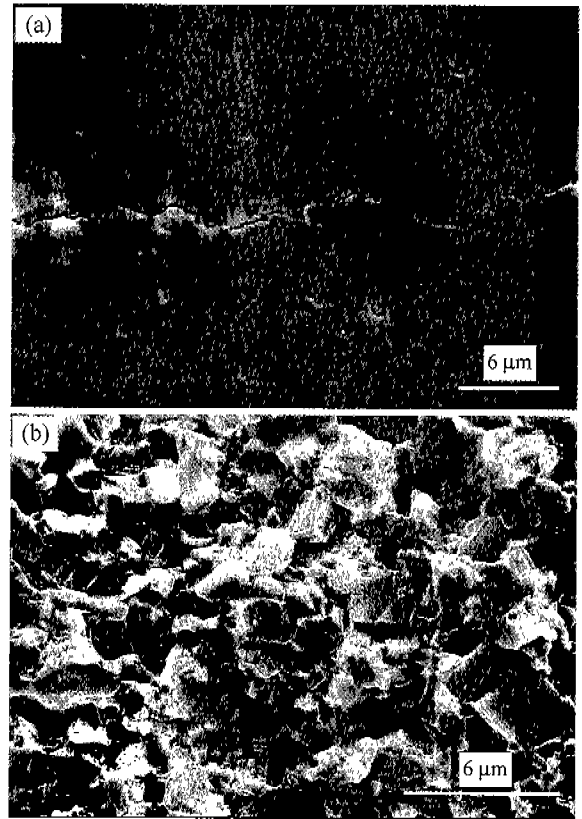

Fig. 3. Typical microstructure and crack path (a) and fracture surface (b) of SiC-TiC composites prepared from SiC-TiC powder. Bright area and dark area corresponds to TiC and SiC phase, respectively. The powder was obtained by the mechanochemical processing of the mixture of 0.5 : 0.5 : 1 of mole ratio of Si : Ti : C.

the formation of TiC for the formation of SiC. It means that the heat of reaction of TiC is important for the formation of SiC. Among the tested composition, the SiC and/or TiC phase has not been observed for the mixtures having composition 0.9 : 0.1 : 1 of the mole ratio of Si : Ti: C. It confirms the role of the formation of TiC on the formation of SiC. The role of formation of TiC could also be confirmed by the fact that relative sharp and strong peaks of TiC and SiC have been observed in the early stage and then it has gradually broadened and weakened with McS time. The sharp and strong peaks indicate the formation of crystallites by the thermal energy as well as the mechanical energy.

Fig. 2 shows the crystallite size of the powders calculated by the Debye-Scherrer equation. Because the broadening of the XRD peaks indicates a decrease in the coherent crystalline domain or crystallite size and an accumulation of lattice strain, the full width at half maximum (FWHM) was used for the size evaluation. Fig. 2 shows that the reduction in size below 10 nm has been achieved mostly in the early stage (i.e., first a few hours) of McS and further reduction in size is not significant. Especially, Fig. 2 (b) shows the curve with a steep slope, which indicates that the exothermic reaction takes place in McS and the formation of TiC crystalline has been preceded very fast. However, the steep slope in the crystalline size has not been observed in the mixture of Si, Ti, and C. It indicates that the formation of SiC and TiC crystallities has been preceded slowly.

Fig. 3(a) shows the typical microstructures of the SiC-TiC composites prepared by hot-pressing of the SiC-TiC powder (mole ratio of Si : Ti : C is 0.5 : 0.5 : 1) at 1850 °C for 3 h. The SiC-TiC composites prepared in this study was two phase particulate composites consisted of interconnected or dispersed TiC grains depending on the amount of TiC whose diameters ranging from 1 to 6 μm in the SiC matrix.

Dense SiC-TiC composites has been obtained from all the composition by hot-pressing. It shows the feasibility of McS for the preparation of powders for easy densification of the materials covalent bonded in nature due to the small crystallite size and highly disordered crystal structure of the powders. It should be noted that the sintering conditions has not been optimized in this study. Therefore, the result of this study remain a possibility for preparing dense SiC-TiC composites with more "mild" hot-pressing conditions or even by pressureless sintering, as shown in TiB_2 based composites.[15]

Variation of flexural strength and fracture toughness of the composites with composition is shown in Fig. 4. For comparison, the strength and toughness of SiC-TiC composites prepared by commercially available SiC and TiC powders with same sintering additives and sintering conditions are inserted in Fig. 4. As shown, the flexural strength and
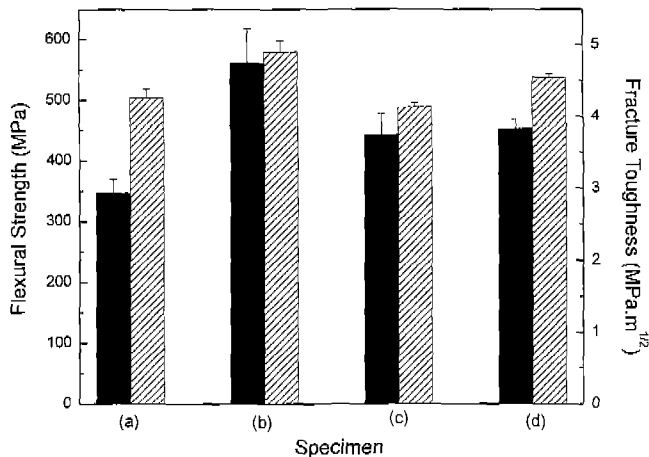
Fig. 4. Flexural strength (filled bars) and fracture toughness (slashed bars) of the composites prepared by hot-pressing of (a) the mixture of 0.9 : 0.1 : 1 of mole ratio of Si : Ti : C, (b) the mixture of 0.75 : 0.25 : 1 of mole ratio of Si : Ti : C, (c) the mixture of 0.5 : 0.5 : 1 of mole ratio of Si : Ti : C, and (d) the mixture of 1 : 1 of mole ratio of commercially available SiC and TiC powder.

fracture toughness have been increased especially by addition of 25% of TiC (i.e., 0.75 : 0.25 : 1 of mole ratio of Si : Ti : C) to 560 MPa and 4.8 MP · am$^{1/2}$, respectively. It is well known that the dispersion of TiC particles in SiC matrix improves the fracture toughness.[1-6] It is claimed that the residual stresses due to the thermal expansion mismatch between TiC (7.4×10^{-6}°C) and SiC (4.8×10^{-6}°C) particles improves toughness by deflecting the cracks around the TiC particles.

Fig. 3 (a) shows the typical crack deflection around the TiC particles, which support the crack deflection mechanism contributing of TiC particles to fracture toughness. Fig. 3 (b) also shows that the intergranular mode of fracture, which indicated weak interface boundaries due to thermal expansion mismatch between SiC and TiC particles. The weak interfacial boundaries leading to the enhanced crack deflection, as shown in Fig. 3 (a).

The increase in flexural strength of the SiC-TiC composites with the addition of TiC may relate to the change of fracture toughness and microstructure. The relationship between fracture strength (σ), fracture toughness (K_{IC}), and critical flaw size (c) can be expressed as $K_{IC} = Y\sigma c^{1/2}$ where Y is a geometric factor. The equation indicates that the flexural strength will increase with increasing fracture toughness and decreasing critical flaw size. Addition of TiC inhibits the grain growth of SiC and it decreases the critical flaw size of the SiC-TiC composites.[16] It also increases the fracture toughness by deflecting the cracks around the TiC particles. Both factors contribute to the increasing flexural strength.

However, addition of TiC more than 25% has degraded the strength and toughness of the composites. It is due to occupation of large amount of TiC, which has inferior

mechanical properties compared to SiC, in the composites. For example, the typical bending strength of TiC (~400 MPa) is lower than that of SiC (~580 MPa).[17] It also increases the critical flaw size of the composites by increasing the size of TiC and it could give an adverse effect on the strength and toughness.[1]

As shown in Fig. 4, the mechanical properties of the SiC-TiC composites prepared via mechanochemical process are comparable to those of the composites hot-pressed with the commercial SiC-TiC powders in the composition of 0.5 : 0.5 : 1 of mole ratio of Si : Ti : C. It should be noted that the hot-pressing conditions for the SiC-TiC composites prepared in this study has not been optimized and, therefore, the properties could be improved by refining the sintering conditions in the future study.

4. Summary

A mixture of SiC and TiC powder has been obtained by mechanochemical process of the mixture of Si, Ti, and C. It has revealed that heat release from the formation of TiC render the formation of SiC, which can not be obtained from the mechanochemical processing of the mixture of Si and C. Mechanical properties of SiC-TiC composites obtained by mechanochemical process followed by hot-pressing are comparable to those of the composites hot-pressed with the commercial SiC-TiC powders.

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