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Grain-Refinement of SiC-ZrO_2 Ceramic Matrix: Characterizations and Its Effect on Mechanical Properties

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Abstract: Silicon carbide with 50 mass% zirconia ceramic matrix composites were processed by Mechanical Milling (MM) followed by Spark Plasma Sintering (SPS). By controlling the parameters of MM and SPS, an ultra-fine ZrO_2 grain was homogeneously dispersed and refined on the surface of a fine SiC powder, forming a harmonic microstructure. The mechanical properties and the densification behavior of the SiC-ZrO_2 composites were investigated. The effects of the milling time on the microstructure and on the mechanical properties of the composite are discussed. The results indicate that the composite mechanically milled for 144 ksec and sintered at 1773 K had the highest relative density of 98% along with a bending strength of 1128 MPa and a fracture toughness of 10.7 MPa.$m^{1/2}$. These superior mechanical properties were influenced by the microstructure characteristics such as the homogeneous grain dispersion. Thus, the grain refinement forming harmonic microstructure can be considered a remarkable design tool for improving the mechanical properties of SiC-ZrO_2 as well as other ceramic composite materials.

Key words: Mechanical milling, spark plasma sintering, SiC-ZrO_2, microstructure, mechanical properties, remarkable design

INTRODUCTION

Silicon Carbide (SiC) is ceramic with either a cubic (β) or hexagonal (α) crystal structure which can be produced by hot-pressed, direct-sintered, reaction-sintered and Chemically Vapor Deposited (CVD) process. Relatively SiC can be fabricated to essentially full density and high strength by using addition of boron and carbon or using addition of alumina (Al_2O_3) to either or α or β-SiC starting powder (Leatherman and Katz, 1989). Hot pressing is typically accomplished at temperatures of 2173-2373 K with pressures of 60 MPa (Leatherman and Katz, 1989). In direct-sintered SiC, submicrometer SiC powder is compacted and sintered at temperatures in excess of 2373 K, resulting in high-purity product as mentioned in the handbook (ASM Handbook). On the other hand, reaction-bonded SiC is processed by forming a porous shape composed of SiC and carbon-powder particles (ASM Handbook). The shape is then infiltrated with silicon metal which bonds the SiC particles. Both direct-sintered and reaction-sintered SiC ceramics have relatively low fracture toughness values of 3-4 MPa.$m^{1/2}$ (ASM Handbook).

SiC-based ceramics are very promising high temperature structural materials owing to their excellent thermal and mechanical properties (Huang and Zhu, 2005). However, monolithic SiC is a highly covalently bonded silicon and carbon compound that is difficult to densify (Kim *et al*., 1998) and its low resistance to fracture has impeded its widespread application.

Furthermore, Zirconium Oxide or Zirconia (ZrO_2) cannot be fabricated into a fully dense ceramic body using conventional and non-conventional powder processing techniques (ASM Handbook). The 3-5 vol.% increase associated wity the tetragonal-to-monoclinic phase transformation causes any pure ZrO_2 body to completely destruct upon cooling from the sintering temperature (ASM Handbook). Additives such as Calcia (CaO), Magnesia (MgO), Yttria (Y_2O_3) or Ceria (CeO_2) must be mixed with ZrO_2 to stabilize the material in either the tetragonal or cubic phase (Basu, 2005). Applications for cubic-stabilized ZrO_2 is include on various oxygen-sensor devices because cubic-ZrO_2 has excellent ionic conductivity, induction heating elements for the production of optical fibers, resistance heating elements in new high-temperature oxidizing kilns and inexpensive diamond like gemstones (Basu, 2005).

Transformation-Toughened Zirconia (TTZ) is a generic term applied to stabilized ZrO_2 systems in which the tetragonal symmetry is retained as the primary phase (Basu, 2005). The most popular tetragonal-phase stabilizers are Y_2O_3, CaO and MgO. TTZ is a high-strength

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material with fracture toughness values ranging from 6-15 MPa.m$^{1/2}$, compared to traditional ceramics with fracture toughness of only about 2-3 MPa.m$^{1/2}$ which can be manufactured by sintering at relatively low temperatures 1673 K (ASM Handbook). The mechanism of toughening in TTZ materials involves a volume increase because of a polymorphic transformation that is triggered when an applied stress causes a crack to form in TTZ (ASM Handbook). The volume increase only occurs for material adjacent to the crack and presses against the crack to keep it from propagating through the TTZ. The toughening mechanism are similar forms on the steel, therefore TTZ has sometimes been called ceramic steel (ASM Handbook). However, among the several approaches that have been used to inhibit the catastrophic failure of various ceramics, toughening by incorporating ZrO_2 in the ceramics matrix has been very successful (Becher *et al*., 1987).

These reinforcements make use of different energy absorbing mechanism (such as crack deflection, crack branching or crack bowing) which becomes operative in the stress field of an advancing crack tip (Becher *et al*., 1987). Based on the background of extensive literature review of ceramic composites led to conclude that in ceramic composite powder processing, the major direction can be applied to toughen silicon carbide and other ceramics for example using the composite technology by incorporating particulate, w hiskers, platelets or fiber. Ceramic-based nanocomposite is one of the particulate-reinforced composites in which the nano-sized particulate is dispersed within the matrix grains and/or at the grain boundaries (Bamba *et al*., 1998). Dispersion of Zirconia (ZrO_2) grains in ceramics is an effective method to enhance the fracture toughness of the matrix either by taking advantage of the stress-induced martensitic transformation of ZrO_2 from the tetragonal to monoclinic phase which absorbs the fracture energy or by crack blending caused by microcracks and residual stress introduced owing to volumetric expansion during cooling of ZrO_2 grains (Dutta and Buzek, 1984).

Although, randomly dispersion of ZrO_2 particles in many ceramics have been previously studied by many researchers, the control formation of the dispersion and its effect on the mechanical properties has also already reported before that the SiC-ZrO_2 microstructure refinement with harmonic grain dispersion indicate superior mechanical properties (Anggraini *et al*., 2011, 2014). Thus, the objective of the present study is to characterize more details the grain refinement and to report its effect of mechanical properties of SiC-ZrO_2 obtained by mechanical milling and spark plasma sintering.

MATERIALS AND METHODS

Experimental procedures: The MM process on the SiC-ZrO_2 was performed with a vibration ball mill with speed of 12.5 Hz. The ball-to-powder weight ratio of 5:1 and the process time from 0 sec to 144 ksec were chosen. Subsequently, the MM powders were sintered in an SPS process.

The controlled SPS temperature and heating rates were 1773 K and 6 K/sec, respectively. These determined temperatures and heating rates were based on our investigation, above these temperatures will result in the grain growth. After the mixtures had been soaked at a desired heating time for 0.6 ksec and the specimens were cooled down to room temperature. Samples sintered by means of SPS measured approximately 15 mm in diameter and 5 mm in thickness.

The impurities of the powders before and after mechanical milling were characterized by X-ray diffraction analysis. The morphology of the grains was investigated using a field-emission scanning electron microscope (FE-SEM S-4800, Hitachi, Japan) and a transmission electron microscope. The sintered samples were cut in half and their cross-sections carefully polished into rectangular bar specimens (2×4×15 mm). The mechanical properties were examined in hardness and bending tests. The hardness was measured with a Shimadzu HMV-1 based on Vickers indentations obtained by applying a 98.1 N load for 10 sec. The measurement was conducted at 30 random points in each specimen. The fracture toughness was measured based on the crack length using Vickers indentation and the equation (Anstis *et al*., 1981). The bending strength was evaluated in room-temperature by means of the three-point bending method with a Shimadzu AG-I-50 kN instrument on 2×4×13 mm specimens with a crosshead speed of 0.5 mm/60 sec.

RESULTS AND DISCUSSION

Figure 1 shows FE-SEM images of SiC-ZrO_2. As shown in the non-milled powder mixture in Fig. 1 (a), the shape of the SiC was irregular and the ZrO_2 was agglomerate. Before mixing, the amount of ZrO_2 grains which attach on the surface of the SiC powders is very limited. As a result of mixture, there is no change in the appearance of both SiC and ZrO_2. From this image, it appears that the grain dispersion is heterogeneous.

After mechanical milling, the surface of the SiC powders becomes finer and almost fully covered with ZrO_2 grains as shown in Fig. 1b. In order to achieve homogeneous grain dispersion, control of the milling time

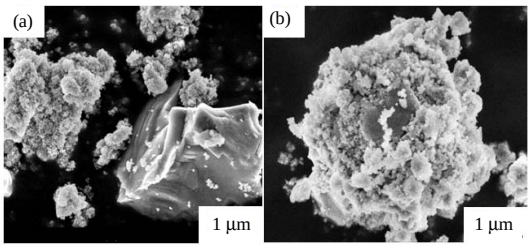

Fig. 1: SEM micrographs of SiC-ZrO_2 powders mechanically milled for: a) 0 sec and b) 144 ksec

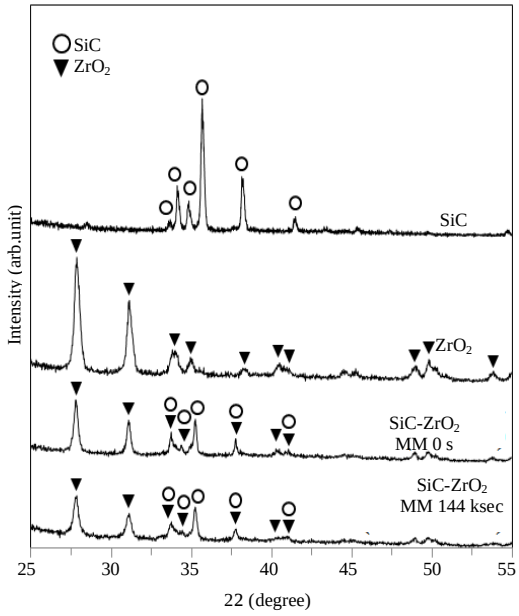

Fig. 2: X-ray diffraction pattern of initial powders (before sintering) CuKα

was very important. If the milling time was too short, the dispersion of ZrO_2 on the surface of SiC would remain heterogeneous. The homogeneous grain dispersion could be fully achieved for a milling time of 144 ksec. The size of the SiC powders was not significantly reduced and their shape became somewhat spherical. In the case of ZrO_2, the size was refined and the shape of the grains was deformed.

The refinement of the grain size is consistent with the broadening of X-ray diffraction peaks in Fig. 2. In the case of the non-milled powder mixture (heterogeneous dispersion), the diffraction peaks were slightly narrower than for the milled powders (homogeneous grain dispersion). According to Scherrer's Eq. 1:

$$\tau = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

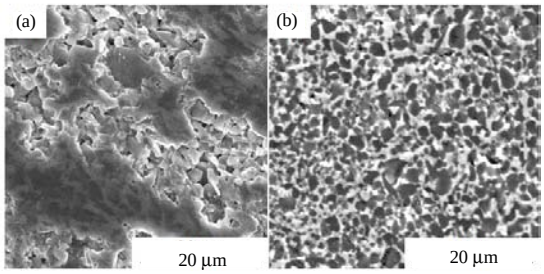

Fig. 3: Cross-sectional SEM micrographs of SiC-ZrO_2 with MM: a) 0 sec and b) 144 ksec

Where:
K = The shape factor
λ = The X-ray wavelength of the radiation used (CuK_α)
β = The line broadening at half the maximum intensity (FWHM) in radians
θ = The Bragg angle
τ = The mean size of the crystalline domains which may be smaller or equal to the grain size

The broadening of diffraction peaks indicates a reduction in crystalline size (Ruan *et al*., 2000). No phase transformation or new phase formation for both SiC-ZrO_2 was found in the non-milled and milled powder mixtures such that SiC and ZrO_2 maintain their cubic and monoclinic structures, respectively.

Figure 3 shows the cross-sectional SEM micrograph of the SPS compacts which were fabricated with milling times, 0 sec and 144 ksec. Generally, the relative density increases with increasing sintering temperature. Moreover, the milling time also has a remarkable influence on the relative density of the sintered composites. As the milling time increased, the relative density of the sintered SiC-ZrO_2 composites also increased at the constant sintering temperatures. However, for powder sintered by hot-pressing, a temperature of at least 1923 K and 3.6 ksec of soaking time are needed. Meanwhile, applying a high temperature and a long sintering time allows grain growth and would eventually produce a low-performance ceramics. With a lower sintering temperature and time, a ceramics with a high density can be obtained. Very few pores were observed on the cross-section of the SiC-ZrO_2 with MM for 144 ksec and the relative density is near 100%.

The effects of milling time on the bending strength and fracture toughness of the SiC-ZrO_2 ceramics matrix composite are shown in Fig. 4. The values in the table reveal that the bending strength and fracture toughness of the SiC-ZrO_2 ceramic matrix composites increased with the milling time. The superior mechanical properties of

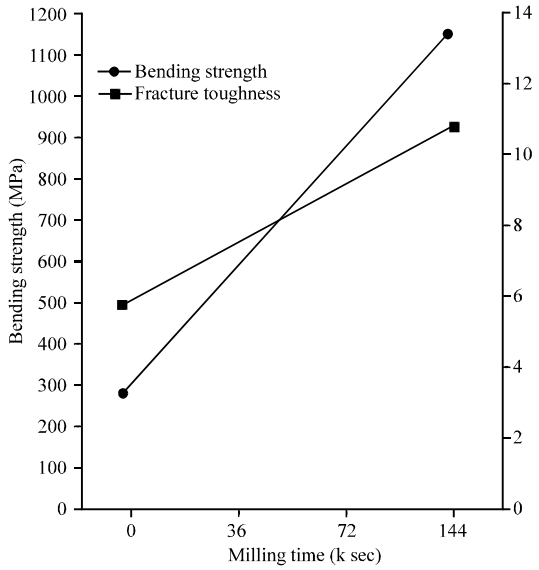

Fig. 4: Effect of milling time on the bending strength and fracture toughness of SiC-ZrO_2

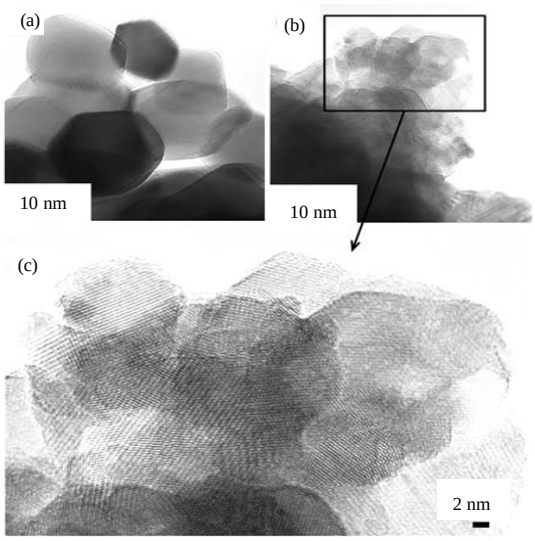

Fig. 5: HRTEM micrographs of ZrO_2 grains: a) Before MM (0 ksec); b) After MM 144 k ecs and c) Enlargement of MM 144 ksec

ceramic matrix composites were obtained on the harmonic dispersion structure specimens with milling time of 144 ksec.

Moreover, other references (Cheloui *et al*., 2011) state that the bending strength and fracture toughness can be improved by increasing the sintering temperature while the high sintering temperature can cause grain growth. Meanwhile, our results show that high mechanical properties can be obtained by increasing the milling time and controlling the micro structure by keeping the temperature for sintering constant and relatively low. Therefore, there is certainly no grain growth.

Figure 5a and b show the high resolution TEM micrographs of the ZrO_2 powder before and after milling for the time 0 and 144 ksec, respectively. These morphological changes are attributed to a fragmentation of the grain agglomerates which was caused by the high energy mechanical milling. The effect of milling time is correlated to the fact that the long milling time produced higher density. From these TEM micrographs, it is also well known that the surface roughness of ZrO_2 powder was deformed by the high-energy mechanical milling. The grain refinement of ZrO_2 successfully achieved after MM 144 ksec. The rough surface cannot be obtained on mechanically milled SiC because the theoretical hardness of SiC is higher than that of ZrO_2. Therefore by grain refinement and controlling the homogeneous dispersion of ZrO_2 on the SiC surface, a high density of ceramic matrix composites can be achieved.

CONCLUSION

The conclusions obtained are as follows: mechanical milling powder, consisting of SiC powder and ZrO_2 grains was sintered by means of spark plasma and the effects of the dispersion of SiC-ZrO_2 on the mechanical properties produced by the MM-SPS process were investigated. The ZrO_2 grains were refined and the dispersions were homogenized on the SiC surface by mechanical milling.Grains refinement was obtained after mechanical milling for 144 ksec. The superior mechanical properties successfully obtained in the harmonic microstructure materials with homogenization of the fine grains dispersion.

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