Effect of Mechanical Milling and Sintering Parameters on the Mechanical Properties of SiC-ZrO$_2$ Composite with a Network Microstructure

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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 on the surface of a fine SiC powder, forming a network 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 40 hours and sintered at 1773 K had the highest relative density of 98 %, along with a flexural 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 particle dispersion. Thus, the network microstructure can be considered a remarkable design tool for improving the mechanical properties of SiC-ZrO$_2$, as well as other ceramic composite materials.

Keywords: Mechanical milling, spark plasma sintering, SiC-ZrO$_2$, microstructure, mechanical properties

I. Introduction

Silicon-carbide (SiC)-based ceramics are very promising high-temperature structural materials owing to their excellent thermal and mechanical properties [1–5]. However, monolithic SiC is a highly covalently bonded silicon and carbon compound that is difficult to densify [6], and its low resistance to fracture has impeded its widespread application.

One major approach is to strengthen and toughen silicon carbide and other ceramics, for example with the use of composite technology by incorporating particulate, whiskers, platelets or fiber [7–11]. 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 [12]. Dispersion of zirconia (ZrO$_2$) particles 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$_2$ particles [13]. ZrO$_2$ has been successfully used as a toughening agent in Al$_2$O$_3$, SiAlON and Si$_3$N$_4$ matrix composites to improve their mechanical properties [14–16]. Clausen and Jahn reported that the addition of 20 vol% unstabilized ZrO$_2$ to an Si$_3$N$_4$ matrix improved the fracture toughness thanks to a microcracking toughening mechanism [14]. They also indicated the formation of Si$_2$ON$_2$. Terao *et al.* found that the dispersion of 20 mass% of 2.5 mol% Y$_2$O$_3$-stabilized ZrO$_2$ in Si$_3$N$_4$ was advantageous to increase the room-temperature fracture toughness without any degradation of hardness [17].

Although random dispersion of ZrO$_2$ particles in many ceramics has been previously studied by many researchers, the controlled formation of the dispersion and its effect on the mechanical properties has not been previously reported in any literature. Thus, the objective of the present study is to investigate the effect of a homogeneous dispersion or a network microstructure of the SiC-ZrO$_2$ controlled by mechanical milling (MM) and spark plasma sintering (SPS) parameters on the mechanical properties. The concept of creating a network microstructure is shown in Fig. 1.
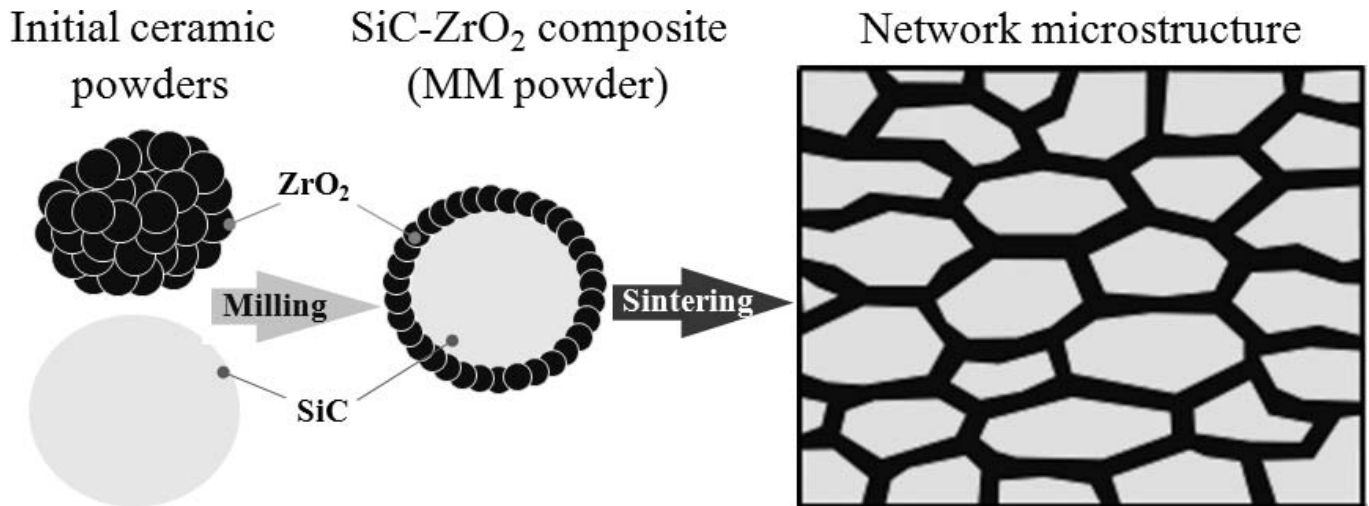
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Fig. 1: Concept of creating a network microstructure.

II. Experimental Procedures

(1) Mechanical milling

Alpha-SiC powders of $2 \sim 3 \, \mu m$ were milled with 50 mass% of 30 nm unstabilized-ZrO_2 powders, commercialized by Kojundo Chemical Laboratory, Co., Ltd. This mixture was used as a starting material and was mechanically milled with a WC-Co ball and pot with a diameter of 5 and 60 mm, respectively. The MM process on the SiC-ZrO_2 powders was performed with a Super Misuni NEV-MA-8 vibration ball mill. This MM process used a vibrating speed of 1600 rpm. In addition, the milling was performed in dry conditions, and no agent was used. The milling intensity can be controlled by selecting the ball-to-powder weight ratio and the process time. The values chosen for these two parameters were 5:1 and from 0 to 40 hours, respectively. Subsequently, the MM powders were sintered in an SPS process.

(2) Sintering parameters

SPS was performed in a vacuum using DR.SINTER 1020 apparatus (SPS Syntex Inc., Japan). The SPS process was performed with a pressing die made of graphite under 50 MPa uniaxial pressure. The external and internal diameters of the die measured 30 mm and 15.5 mm, respectively, and the height of the cylindrical graphite die was 30 mm. The diameter and the height of the graphite punch were 15 mm and 20 mm, respectively. The temperature was measured using an infrared active homing (IR-AH) thermometer through a thermometer hole with a diameter of 0.5 mm and a depth of 20 mm located in the center of the die. The controlled sintering temperature and heating rates were 1773 K and 373 K per minute, respectively. After the mixtures had been soaked at a desired milling time for 10 min, the applied current was cut off, the pressure was released, and the specimen was cooled down to room temperature. Samples sintered by means of SPS measured approximately 15 mm in diameter and 5 m in thickness.

(3) Characterization tests

The sintered samples were cut and carefully polished into rectangular bar specimens (2 mm × 4 mm × 15 mm). The microstructure of the materials was characterized by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The bulk density was measured with the image analysis software (Analy-SIS FIVE, digital imaging solution) because there was no theoretical density of the SiC-ZrO_2 composite available. The mechanical properties were examined in hardness and bending tests. The hardness and the fracture toughness were measured with an Akashi AVK-C2 based on Vickers indentations obtained by applying a 98.1 N load for 10 s. 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 Anstis *et al.* equation [18]. The flexural strength was evaluated by means of the three-point bending method with a Shimadzu AG-I-50kN instrument on 2 mm × 4 mm × 13 mm specimens, with a crosshead speed of 0.5 mm/min.

III. Results

(1) Microstructure of MM-SPS compacts and relative density

Figs. 2(a) and (b) show SEM micrographs of SiC and ZrO_2 powders, respectively, before mechanical milling. The initial SiC powder shows an irregular shape and an agglomeration in the initial ZrO_2 powder. After manual mixing for 0 hours and mechanical milling for 5, 15, 20 and 40 hours, the SiC powder surface became increasingly covered with ZrO_2 powder, as shown in Figs. 3(a) – (e). In order to achieve homogeneous dispersion, control of the milling time was very important. If the milling time was too short, the dispersion of SiC and ZrO_2 would become heterogeneous, resulting in lower mechanical properties than expected. Thus, with the milling time of 40 hours, homogeneous particle dispersion could be fully achieved.
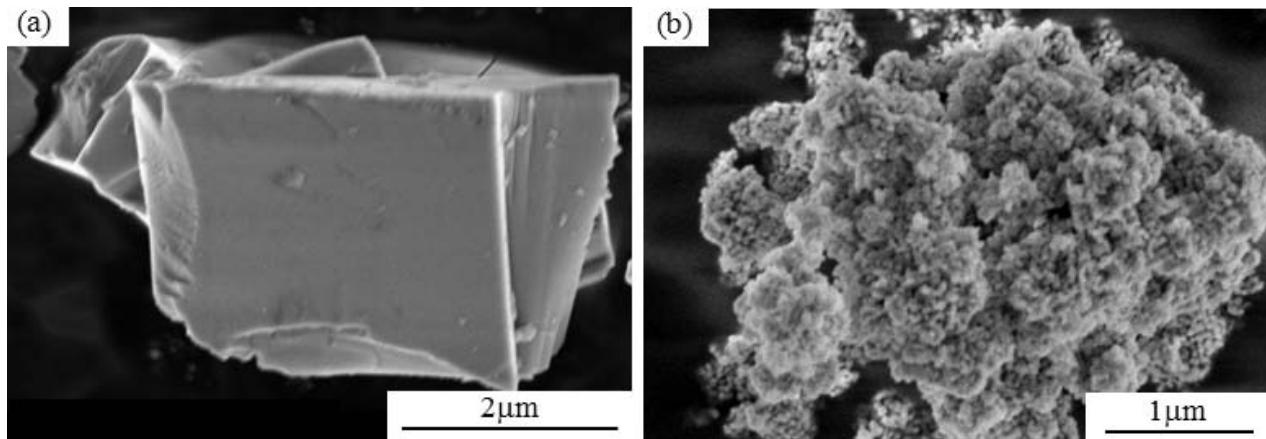
Fig. 2: SEM micrographs of the initial (a) SiC and (b) ZrO$_2$ powders.
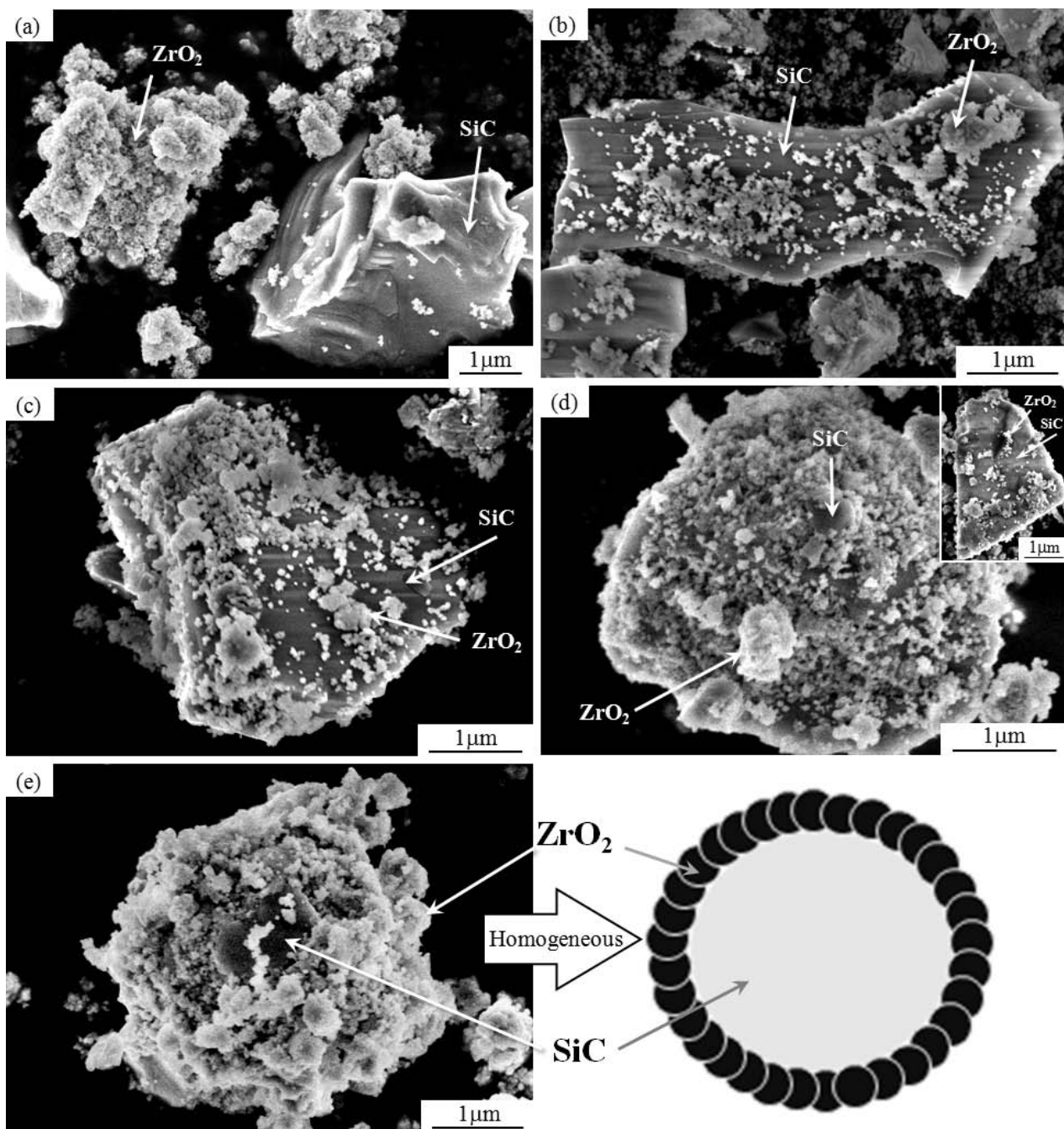

Fig. 3: SEM micrographs of SiC-ZrO$_2$ powders mechanically milled (MM) for (a) 0 hours (b) 5 hours (c) 15 hours (d) 20 hours, and (e) 40 hours.

Figs. 4(a)–(e) show cross-sectional SEM micrographs of the SPS compacts, which were fabricated with various milling times, from 0 to 40 hours, respectively. 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 1 hour 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 ceramic. Therefore, using mechanical milling and the spark plasma sintering process, with a lower sintering temperature and a lower sintering time, a ceramic with a high density can be obtained. Very few pores were observed on the cross-section of the SiC-ZrO$_2$ with MM for 20 and 40 hours, indicating that a dense composite can be prepared by the MM-SPS process even at low sintering temperatures. Correspondingly, the relative densities of SiC-ZrO$_2$ with MM for 20 and 40 hours were near 100 % for both specimens.
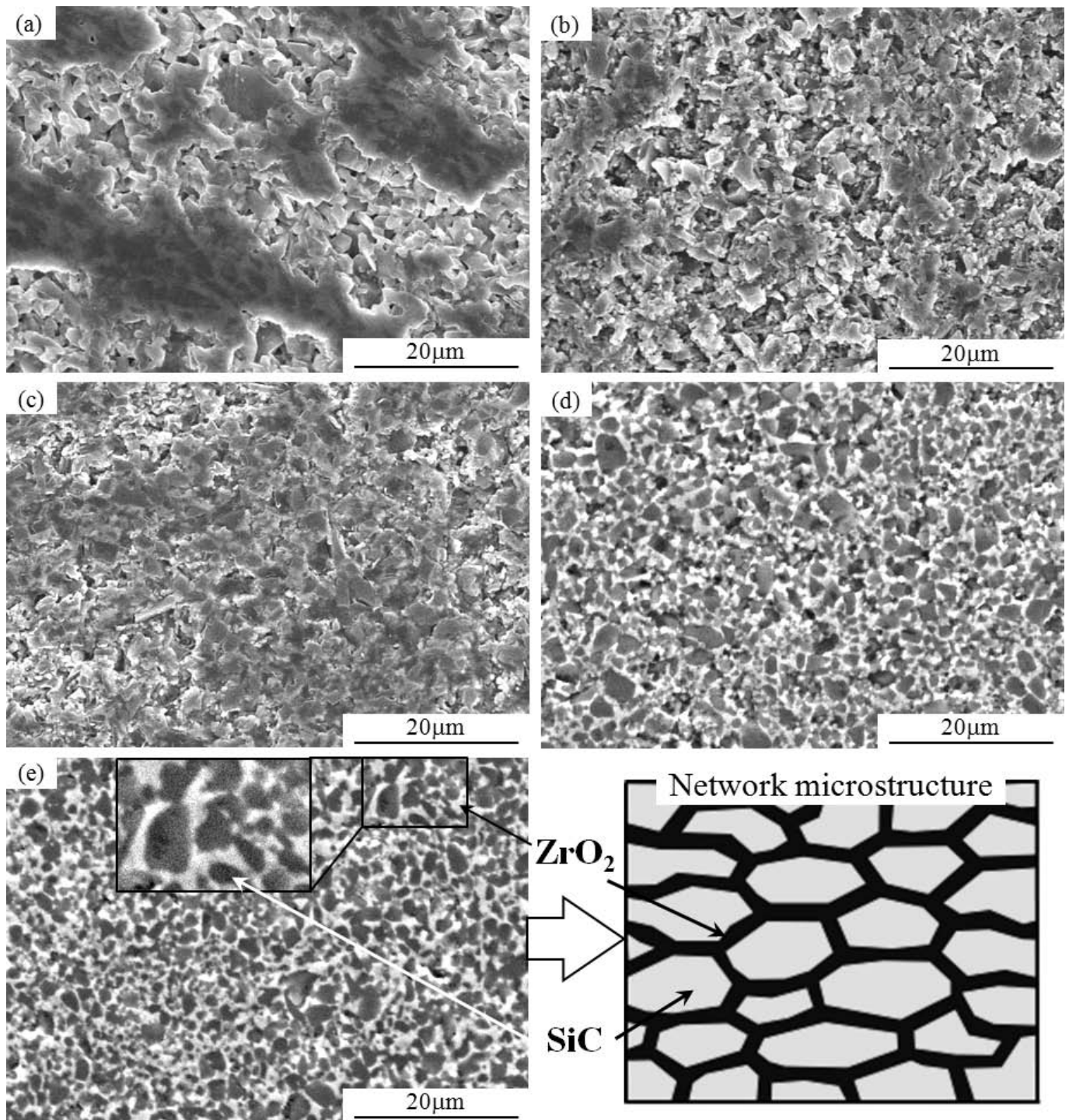

Fig. 4: Cross-sectional SEM micrographs of (a) MM 0 hour, (b) MM 5 hours, (c) MM 15 hours, (d) MM 20 hours, and (e) MM 40 hours.

Table 1: Summary of the mechanical properties of SiC-ZrO$_2$ materials including the standard deviation.

Material	Additive	Milling time (hrs)	Micro-Vickers hardness (H_v)	Flexural strength (MPa)	Fracture toughness (MPa·m^{12})
SiC	50mass%ZrO$_2$	0	1104+33.2	266±16.3	5.7±0.19
SiC	50mass%ZrO$_2$	5	1102±33.2	250±15.8	5.3±0.17
SiC	50mass%ZrO$_2$	10	1108±33.3	273±16.5	5.9±0.24
SiC	50mass%ZrO$_2$	15	1167±34.2	275±16.6	6.8±0.24
SiC	50mass%ZrO$_2$	20	1515±38.9	690±26.3	8.5±0.35
SiC	50mass%ZrO$_2$	40	1687±41.1	1128±33.5	10.7±0.39
SiC	50mass%ZrO$_2$	100	1598±39.9	992±31.4	9.3±0.36

(2) *Mechanical properties of SiC-ZrO$_2$*

The effects of milling time on the hardness, flexural strength and fracture toughness including the standard deviations of the SiC-ZrO$_2$ composite are shown in Table 1. The values in the table reveal that the hardness, flexural strength, and fracture toughness of the SiC-ZrO$_2$ composites increased with the milling time. Moreover, the addition of 50 mass% ZrO$_2$ to the mixtures increased the strength and the toughness of the monolithic SiC ceramic by more than 100 % [19]. Because the densification temperature of the pure SiC ceramic is near 2173 K [19], SiC grains will grow in the sintering process. Thus, the decrease in the mechanical properties is attributed to the grain growth [20]. When 50 mass% ZrO$_2$ were added to the initial SiC powders, the densification temperature was decreased to ~ 1973 K. As the grain size of ZrO$_2$ is smaller than that of SiC the composite becomes easier to sinter. When the milling time was increased to 40 hours, the densification temperature of the composite further decreased because of the finer dispersion of ZrO$_2$ produced after the high-energy mechanical milling process. Then, the SiC ceramic with homogeneous fine grains of ZrO$_2$ dispersed on its surface was obtained, and the mechanical properties were improved. It is noted that the sintering temperature depends strongly on agglomerate size [23]. However, the longest milling time of 100 hours resulted in lower mechanical properties because of the heterogeneous ZrO$_2$ dispersed half on the SiC surface with the other half of the ZrO$_2$ forming a separate agglomeration, which was not helpful in improving the strength and toughness of the SiC. Thus, the dispersion control of ZrO$_2$ and SiC powders with a combination of MM and SPS with appropriate processing parameters plays an important role in improving the mechanical properties of ceramic composites.

The mechanical behavior test results indicated that the relative density of the SiC-ZrO$_2$ sintered at 1773 K is 98 %, the flexural strength of the SiC-ZrO$_2$ is 1128 MPa, and the fracture toughness of the SiC-ZrO$_2$ is 10.7 MPa·m$^{1/2}$. The better mechanical properties of the SiC-ZrO$_2$ composites obtained in this investigation are slightly higher than the other references [19–22]. This dif-ference may be caused by the different starting powders, sintering and testing conditions, as well as the different microstructures.

IV. Discussion

Figs. 5(a) and (b) show the TEM micrographs of the ZrO$_2$ powder before and after milling for the time 0 and 40 hours, respectively. 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 rough surface cannot be obtained on mechanically milled SiC because the theoretical hardness of SiC is higher than that of ZrO$_2$ [24]. Therefore, by controlling the homogeneous dispersion of ZrO$_2$ on the SiC surface, a high density of composites can be achieved.

Fig. 6 shows the relationship of the relative density and the flexural strength of the SiC-ZrO$_2$ composite. For comparison, Fig. 6 includes the published data after processing of monolithic SiC [19] and several composites such as SiC-Al$_2$O$_3$-Yb$_2$O$_3$ [20], SiC-Al$_2$O$_3$-Y$_2$O$_3$ [21], and TiB-TiB$_2$ [22]. The solid line represents a relation delineated through the points obtained by mechanical milling and spark plasma sintering for SiC-ZrO$_2$ materials. It is noted that MM-SPS processing provides two important advantages. First, the strength of SiC is significantly improved by ZrO$_2$ homogeneous dispersion so that it becomes comparable to the flexural strength and even better density of mechanically milled SiC-ZrO$_2$ after spark plasma sintering. Second, the SiC-ZrO$_2$ powders processed by mechanical milling for 40 hours showed the highest strength after MM-SPS when compared with other materials. The microstructure and processing methods are shown in Fig. 6. Moreover, all references state that the density can be improved by increasing the sintering temperature, while the high sintering temperature can cause grain growth. Meanwhile, our results show that high density can be obtained by increasing the milling time and controlling the microstructure by keeping the temperature for sintering constant and relatively low. Therefore, there is certainly no grain growth.
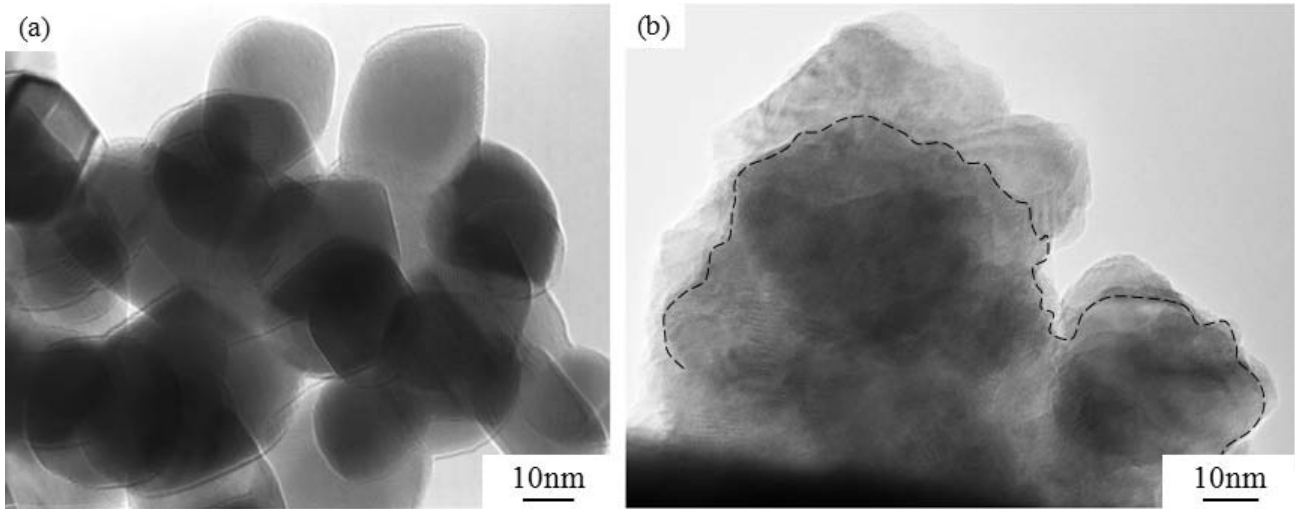
Fig. 5: TEM nanographs of ZrO_2 powders (a) before MM (0 hours) and (b) after MM 40 hours.
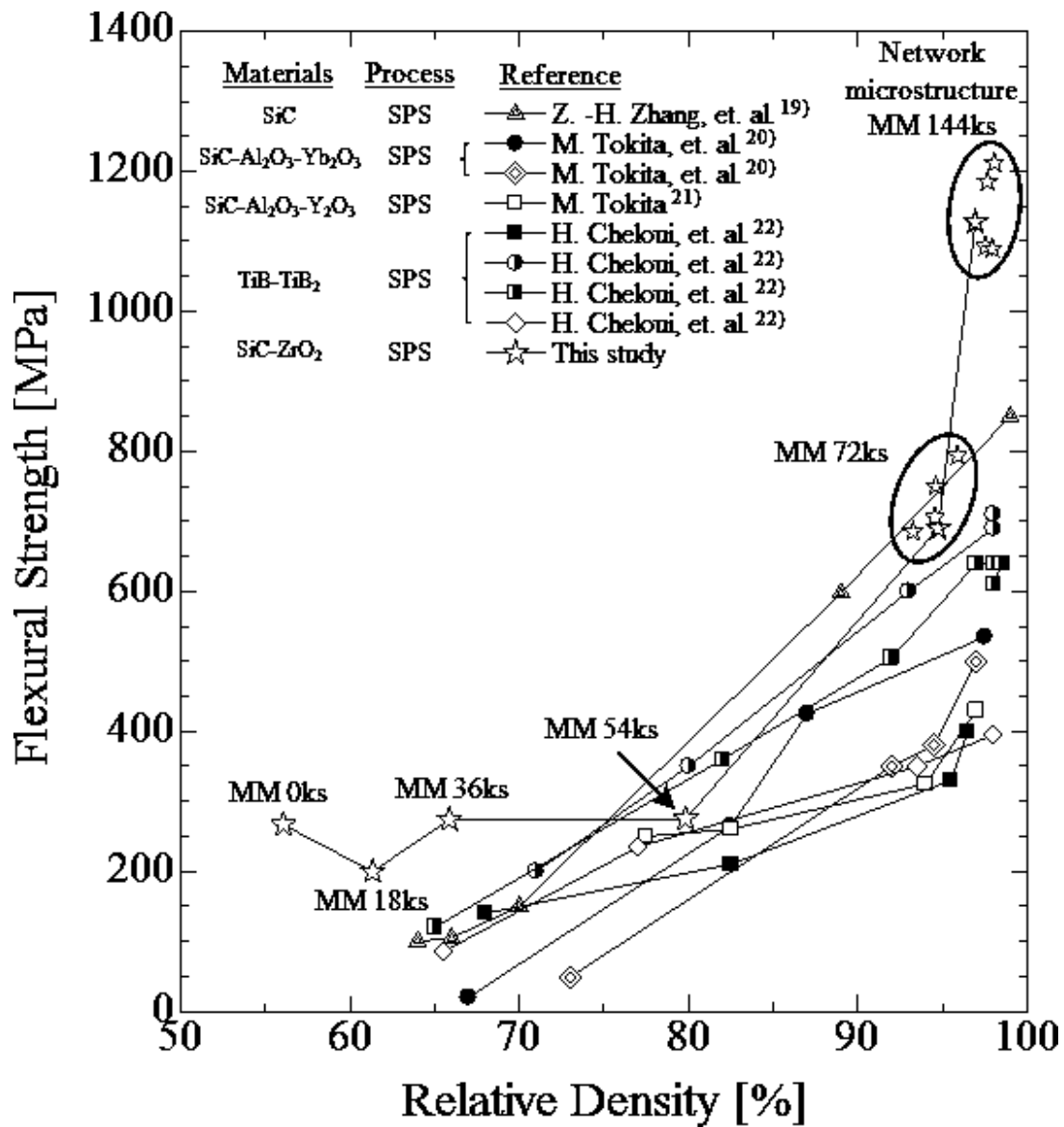

Fig. 6: Plots of the relationship between the flexural strength and the relative density of SPS compacts, including published data for samples of monolithic SiC, SiC-Al_2O_3-Yb_2O_3, SiC-Al_2O_3-Y_2O_3, and TiB-TiB_2 with different microstructures [19–22].

In addition, for the MM 40 hours specimens with a network microstructure, the crack is intergranular which is only in the ultra-fine ZrO_2, and there is no crack in the fine SiC structure. The role of fine SiC grains in the crack deflection is as a locking and disturbing mechanism in the crack propagation along ZrO_2 grains. Therefore, this network microstructure design plays a key role in improving the fracture toughness. The further crack phenomena on this network microstructure will be studied in our future research.

V. Conclusions

Mechanical milling powder, consisting of SiC powder and ZrO_2 particles, was sintered by means of spark plasma, and the effects of the dispersion of SiC-ZrO_2 on the densification behavior and on the mechanical properties produced by the MM-SPS process were investigated. The conclusions obtained are as follows:

(1) By controlling the MM parameters, an ultra-fine ZrO_2 grain homogeneously dispersed on the surface of the fine SiC powder was produced.

(2) By controlling the SPS parameters, a network microstructure was obtained with a density close to 100 %.

(3) The flexural strength can be improved by controlling the microstructure obtained in the high-density materials. Those composites with high density were obtained by controlling the intensity of MM. Therefore, the main factors explaining the improvement in the mechanical properties are considered to be the density increase caused by MM and the homogenization of the dispersion.

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