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# Microstructure and mechanical properties of nano ZrO<sub>2</sub>-10 vol.% TiN composite fabricated by spark plasma sintering

Chun-Feng Hu<sup>a,\*</sup>, Byung-Nam Kim<sup>a,\*</sup>, Young-Jo Park<sup>b</sup>, Koji Morita<sup>a</sup>, Hidehiro Yoshida<sup>a</sup>, Salvatore Grasso<sup>c</sup>, Hai-Bin Zhang<sup>d</sup>, Shu-Qi Guo<sup>a</sup> and Yoshio Sakka<sup>a</sup>

<sup>a</sup>Advanced Materials Processing Unit, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan

<sup>b</sup>Korea Institute of Materials Science, 797 Changwondaero, Changwon 642-831, Republic of Korea

<sup>c</sup>School of Engineering and Material Science, Queen Mary University of London, London E1 4NS, United Kingdom

<sup>d</sup>Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China

Nano ZrO<sub>2</sub>-10 vol.% TiN composite was fabricated by spark plasma sintering (SPS) using nano sized 3Y-ZrO<sub>2</sub> and TiN particles as initial materials. The effects of sintering temperature of 1100-1300 °C, heating rate of 2-250 °C/min, annealing time of 5-120 min, and applied pressure of 20-100 MPa on the microstructure and mechanical properties were systemically investigated. It was confirmed that the main compositions of densified composites were t-ZrO<sub>2</sub> and c-TiN. Both the sintering temperature above 1100 °C and the applied pressure above 60 MPa were the most important factors to affect the full densification of composites. The grain sizes of ZrO<sub>2</sub> and TiN were kept below 243 and 171 nm, respectively. Vickers hardness of 13.90-15.53 GPa, fracture toughness of 2.91-5.44 MPa · m<sup>1/2</sup>, and Young's modulus of 216.2-228.0 GPa of dense composites ascribed to the sintering parameters were discussed.

Key words: ZrO<sub>2</sub>, TiN, Composite, Spark plasma sintering, Microstructure, Properties.

## Introduction

ZrO<sub>2</sub> ceramics have been widely investigated due to their excellent combination of physical and mechanical properties, including high hardness, high fracture toughness, high flexural strength, high wear resistance, and excellent chemical inertia against the acid and alkali environments [1-5]. They have been used as the antiwear parts, cutting tools, high temperature supports, and anti-corrosion valves, etc.. The fabrication of ZrO2 composites has been proved as one effective route to increase the hardness and consequently decrease the wear rate. To date, several composites such as ZrO<sub>2</sub>-WC, ZrO<sub>2</sub>-TiB<sub>2</sub>, ZrO<sub>2</sub>-ZrC, ZrO<sub>2</sub>-SiC, ZrO<sub>2</sub>-TiN, and ZrO<sub>2</sub>-TiCN have been fabricated aiming to achieve an unique combination of high hardness, high strength, and high fracture toughness [6-11]. For example, starting from the powder mixture of nanometric WC and 2Y-ZrO<sub>2</sub>, Vleugels et al. consolidated ZrO<sub>2</sub>-40 vol.% WC composite using pulsed electric current sintering at 1450 °C under a pressure of 60 MPa. Their composite resulted in the high Vickers hardness of 16.2 GPa and flexural strength of 1982 MPa [6]. K. Bonny et al. introduced microsized TiN particles in a 3Y-ZrO2 matrix. They demonstrated that ZrO<sub>2</sub>-40 vol.% TiN composite densified by hot pressing had the high Vickers hardness of 13.44 GPa and fracture

toughness of 5.6 MPa  $\cdot$  m<sup>1/2</sup> [10]. Also, Lauwers *et al.* investigated the effects of nanosized and microsized TiCN, WC, TiC powders (in the composition range of 60/40 vol.%) on the mechanical properties of ZrO<sub>2</sub>based composites. All of the fabricated composites exhibited the high Vickers hardness above 11.16 GPa and fracture toughness above 4.7 MPa  $\cdot$  m<sup>1/2</sup> [11]. However, seldom works have been focused on the fabrication and property evaluation of nano sized TiN particle reinforced ZrO<sub>2</sub> composite. Also, the systematic effects of sintering parameters on the microstructure and mechanical properties of nano sized ZrO2-TiN composite have not been investigated.

In this work, nano ZrO<sub>2</sub> composite containing 10 vol.% TiN was selected as reference composition considering the homogeneous dispersion of TiN nano particles in the composite. In present preparation condition, we confirmed that the larger content of TiN above 10 vol.% would cause the agglomeration owing to the dispersed difficulty of nano particles. Microstructure and mechanical properties of composites prepared under the different processing parameters such as sintering temperature, heating rate, dwelling time, and applied pressure were investigated. The possible reasons controlling the relationship among property-microstructure-process were discussed.

### **Experimental Procedure**

Commercial 3Y-ZrO<sub>2</sub> (27 nm, Tosoh Corp., Japan) and TiN (20 nm, Hefei Kaier Nano Energy Tech Co.,

<sup>\*</sup>Corresponding author: Tel:+81-29-859-2505

E-mail: chfhu@live.cn, kim.byung-nam@nims.go.jp

Ltd, China) particles were used as initial materials to fabricate ZrO<sub>2</sub>-10 vol.% TiN composite. The powders were weighed by an electronic scale with an accuracy of  $10^{-3}$  g and put into a resin jar. The powders were powerfully mixed in a planetary mixer (ARE-250, Thinky Corp., Japan) using ethanol as the dispersing media. Homogeneous mixture was obtained under a high rotating speed of 2000 rpm for 30 min. After milling, the slurry was dried in an oven at 70 °C and then sieved using a 125 mesh sieve. Then the mixture was put into a graphite die with a diameter of 15 mm for pre-compaction under a pressure of 5 MPa. A layer of flexile graphite paper (~ 0.2 mm thickness) was preset into the inner wall of die for lubrication and filling the gap between punches and die, and the die was wrapped using a layer of carbon fiber for inhibiting the rapid heat diffusion. After that the green together with the die was heated in a spark plasma sintering apparatus (100 kN SPS-1050, Syntex Inc., Japan) in vacuum (7 Pa). Each pulse lasted 3.3 ms and the duty cycle was 12 pulses on and 2 pulses off. The temperature was measured by an optical pyrometer focusing on a hole in the wall of die. Below 900 °C, the heating rate was kept at 50 °C/min. During the heating the pressure was slowly increased and it was fully applied starting from 900 °C. The detailed sintering parameters were designed and listed in Table 1. The prepared samples were numerically labelled as ZT01-16. The sintering displacement versus temperature was recorded simultaneously and at last corrected using a known thermal expansion of graphite die. After power off, the sample was cooled down to 900 °C with a rate of 20 °C/min and the pressure was released slowly for inhibiting the appearance of cracks in the composite. Then the temperature was decreased down to ambient with

Table 1. Sintering parameters of ZrO<sub>2</sub>-10 vol.% TiN composite.

Samples	Temperature (°C)	Heating rate (°C/min)	Applied pressure (MPa)	Holding time (min)
ZT01	1100	10	80	20
ZT02	1150	10	80	20
ZT03	1200	10	80	20
ZT04	1300	10	80	20
ZT05	1150	50	80	5
ZT06	1150	50	80	20
ZT07	1150	50	80	60
ZT08	1150	50	80	90
ZT09	1150	50	80	120
ZT10	1150	2	80	20
ZT11	1150	125	80	20
ZT12	1150	250	80	20
ZT13	1150	50	20	20
ZT14	1150	50	40	20
ZT15	1150	50	60	20
ZT16	1150	50	100	20

the cooling rate of furnace.

After removing surface contaminations by a diamond grinding wheel, the samples were ground and polished down to 1.0 mm using the diamond slurries. The density was measured by the Archimede's method. The phase compositions of composite were detected by a Xray diffraction (XRD) analyzer (JDX-3500, JEOL Ltd, Japan) with Cu Ka radiation. The Vickers hardness measurement was conducted by a microhardness tester (MVK-E, Akashi Co., Japan) under a load of 9.8 N. The fracture toughness evaluation was done by an indentation microfracture (IM) method using a hardness tester (AVK-A, Akashi Co., Japan) to induce the diagonal cracks under a load of 49 N. Seven indents were induced and the lengths of diagonal cracks were measured by a scanning electron microscope (SEM) (JSM-6500, JEOL Ltd, Japan). The polished surface of composites was thermal etched at 1000 °C in vacuum ( $10^{-3}$  Pa) for 1 hour. In order to calculate the mean grain sizes of ZrO<sub>2</sub> and TiN, the etched surface of composites was observed by a SU8000 SEM (HITACHI Corp., Japan) and 50 grains were measured. Also, the fracture surface of composites was observed by the SU8000 SEM to determine the damage mechanisms. The Young's modulus was determined by an ultrasonic equipment (TDS 3034B, Tektronix Inc., USA) [12]. For each sample, it was tested for three times.

## **Results and Discussion**

Fig. 1 shows the displacement profiles of ZrO<sub>2</sub>-TiN composite sintered at the different temperature, heating rate, and pressure. Fig. 1(a) exhibits the effect of sintering temperature on the displacement at a heating rate of 10 °C/min, pressure of 80 MPa, and dwelling time of 20 min. It is observed that above 900 °C the densification of composite accelerated with the increasing temperature. Above 1100 °C, the displacement saturated, indicating the near full densification of composite. As listed in Table 2, the measured relative density of ZT01 is high as 99%. When the sintering temperature was increased up to 1300 °C, the displacement did not change more with the increment of temperature, meaning the full densification. The measured relative densities of ZT02-04 were 99.9%, 100%, and 100%, respectively. Additionally, the effect of heating rate in the range of 2-250 °C/min on the densification process is shown in Fig. 1(b). At the sintering temperature of 1150 °C, applied pressure of 80 MPa, and annealing time of 20 min, the lowest heating rate of 2 °C/min resulted in the earlier appearance of constant displacement. Probably, the slow heating rate corresponded to the long heating time, which benefited the more effective grain boundary diffusion [13]. For all of the composites, the relative densities are above 99.9%. In addition, the pressure ranging from 20 to 100 MPa was investigated to account its effect on the densification behavior (Fig.

Samples	Relative density (%)	Vickers hardness (GPa)	Fracture toughness (MPa $\cdot$ m <sup>1/2</sup> )	Young's modulus (GPa)
ZT01	99	$14.84\pm0.57$	$3.22\pm0.11$	216.16
ZT02	99.9	$14.37\pm0.17$	$5.44 \pm 1.05$	220.11
ZT03	100	$14.71\pm0.40$	$3.18\pm0.08$	222.17
ZT04	100	$13.90\pm0.40$	$3.84\pm0.15$	226.39
ZT05	99.8	$15.53\pm0.44$	$4.57\pm0.90$	223.39
ZT06	99.9	$14.87\pm0.27$	$3.70\pm0.45$	221.88
ZT07	100	$14.91\pm0.29$	$3.84\pm0.10$	226.25
ZT08	100	$14.74\pm0.29$	$3.40\pm0.11$	228.04
ZT09	100	$14.58\pm0.34$	$4.50\pm0.66$	226.54
ZT10	100	$14.83\pm0.15$	$4.51\pm0.07$	226.46
ZT11	99.9	$14.96\pm0.52$	$3.61\pm0.27$	221.94
ZT12	99.9	$15.04\pm0.30$	$3.54\pm0.18$	224.33
ZT13	89.7	$9.45\pm0.25$	$3.78\pm0.24$	153.65
ZT14	97.6	$13.79\pm0.31$	$2.62\pm0.19$	213.32
ZT15	100	$15.27\pm0.54$	$3.84\pm0.31$	224.57
ZT16	99.9	15.20±0.83	2.91±0.14	224.70

**Table 2.** Typical physical and mechanical properties of ZrO<sub>2</sub>-10 vol.% TiN composite sintered under the different parameters.



**Fig. 1.** Densification curves of  $ZrO_2$ -10 vol.% TiN composite sintered (a) at the different temperature, (b) under the different heating rate, and (c) under the different applied pressure.

1(c)). The sintering temperature of 1150 °C, heating rate of 50 °C/min, and annealing time of 20 min were chosen. It is clearly observed that when the higher pressure was used the displacement was prone to reach a constant. The pressure of 60 MPa showed the critical level to induce the densification of composite. This result was proved by the measured relative densities of



**Fig. 2.** X-ray diffraction (XRD) patterns of sintered ZrO<sub>2</sub>-10 vol.% TiN composite (a) at the different temperature, (b) with the different heating rate, (c) with the different holding time, and (d) under the different applied pressure.

ZT13 (20 MPa pressing, 89.7%) and ZT14 (40 MPa pressing, 97.6%) which were lower than that of ZT15 composite (60 MPa pressing, 100%). Also, the effect of dwelling time from 5 to 120 min on the densification procedure was investigated by keeping the sintering temperature at 1150 °C, heating rate of 50 °C/min, and applied pressure of 80 MPa. In all of the cases, the relative densities of composites exceeded 99.8%. Therefore, the sintering temperature above 1100 °C and the applied pressure above 60 MPa are the most significant parameters affecting the densification of  $ZrO_2$ -TiN composite. The heating rate and annealing time have the weak influence on the densification process.

Figs. 2(a)-(d) display the X-ray diffraction (XRD) spectra of ZrO<sub>2</sub>-TiN composite sintered under the different temperature, heating rate, holding time, and applied pressure. In comparison with the initial mixture powder where c-TiN, t-ZrO<sub>2</sub>, and m-ZrO<sub>2</sub> could be detected (not shown), all of the sintered samples mainly contained t-ZrO<sub>2</sub> and c-TiN phases. It means that the high temperature sintering promoted the phase transformation from m-ZrO<sub>2</sub> to t-ZrO<sub>2</sub> [14]. It has been known that the sufficient thermal energy supplied to the particles could release the stress and strain so that the monoclinic ZrO<sub>2</sub> is back converted to tetragonal ZrO<sub>2</sub> with the volume contraction of unit cell [15]. In present work, it is supposed that the phase transformation occurred in the temperature range of 900-1100 °C that was corresponding to the rapid increase of displacement (Fig. 1(a)).

Fig. 3 shows the scanning electron microscope (SEM) micrographs of thermal etched surface of  $ZrO_2$ -TiN composites sintered under the different conditions (Table 1). It is observed that the TiN particles (dark



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**Fig. 3.** Scanning electron microscope (SEM) micrographs of thermal etched surface of ZrO<sub>2</sub>-10 vol.% TiN composite sintered at the different parameters: (a) 1100 °C (ZT01), (b) 1300 °C (ZT04), (c) 5 min holding (ZT05), (d) 120 min holding (ZT09), (e) 2 °C/min (ZT10), and (f) 250 °C/min (ZT12).

color) were homogeneously dispersed in the zirconia matrix and mainly located at the grain boundaries of ZrO<sub>2</sub> grains. No obvious pores could be seen in the dense composites, confirming the full densification. Compared to the ZT01 composite sintered at 1100 °C, the grain sizes of ZrO<sub>2</sub> and TiN were larger in the ZT04 composite prepared at 1300 °C, as shown in Figs. 3(a) and (b). By increasing the temperature from 1100 °C to 1300 °C, the grain sizes of ZrO<sub>2</sub> and TiN increased from 122 and 56 nm up to 243 and 171 nm, respectively. Also, when the holding time was increased from 5 min to 120 min, the as-obtained ZT09 composite contained the larger grain sizes of ZrO<sub>2</sub> and TiN (Figs. 3(c) and (d)). The grains of ZrO<sub>2</sub> and TiN grew from 127 and 74 nm to 237 and 121 nm, respectively. These results confirm the increase of grain boundaries' diffusion at the higher sintering temperature and longer annealing time [16]. Additionally, the ZT10 composite prepared at the heating rate of 2 °C/min had the finer grains (ZrO<sub>2</sub> and TiN, 133 and 73 nm) compared to ZT12 sample sintered at the rate of 250 °C/min (ZrO2 and TiN, 163 and 88 nm) (Figs. 3(e) and (f)). B.N. Kim et al. determined that in the Al<sub>2</sub>O<sub>3</sub>-based composite the mechanisms of grain growth and grain boundary slipping were strongly related to the grain boundary diffusion [17-19]. Probably, during the spark plasma sintering under the high pressure, the higher heating rate is associated with the higher power supply of electrical current which might accelerate the atom diffusion of ZrO<sub>2</sub> at the grain boundaries [20-22].

The thermal etched surface and fracture surface of  $ZrO_2$ -TiN composites sintered under the different



**Fig. 4.** SEM micrographs of thermal etched surface and fracture surface of ZrO<sub>2</sub>-10 vol.% TiN composite sintered at 1150 °C under the different pressure: (a) and (c) 40 MPa, (b) and (d) 100 MPa.



**Fig. 5.** Grain sizes of  $ZrO_2$  and TiN as the function of sintering parameters: (a) sintering temperature, (b) dwelling time, (c) heating rate, and (d) applied pressure.

pressure are shown in Figs. 4(a)-(d). As confirmed in Fig. 4(a), the applied pressure of 40 MPa (ZT14) could not induce the full densification. The closed pores were distributed at the grain boundaries of  $ZrO_2$ . Fig. 4(c) evidences the main intergranular fracture mode, confirming the weak bonding of ZrO<sub>2</sub> grain boundaries. Under the high pressure of 100 MPa, the full dense composite (ZT16) without pores could be fabricated (Fig. 4(b)). The multiple transgranular and intergranular fractures were corresponding to the improved grain adhesion under the increased pressure (Fig. 4(d)). Interestingly, it is found that the higher pressure contributed to the grain growth of ZrO<sub>2</sub>. The grain size of ZrO<sub>2</sub> in ZT16 composite is 174 nm, which is significantly larger than that in ZT14 composite (110 nm). This is possibly due to the higher atom diffusion induced by the grain boundary sliding [23, 24].

In order to clearly describe the dependency of grain size on sintering parameter for both  $ZrO_2$  and TiN, the mean particle sizes were calculated by observing the etched surface. Figs. 5(a)-(d) show the grain sizes of

 $ZrO_2$  and TiN as the function of sintering temperature, annealing time, heating rate, and applied pressure. Apart from some deviations, the grain size of  $ZrO_2$  tends to increase by increasing the sintering temperature, holding time, heating rate, and pressure. However, the weak tendency is observed for TiN particles. Especially, the growth of TiN is insensitive to the applied pressure (Fig. 5(d)). This is possibly ascribed to the higher activation energy for diffusion and the lower sinterability of TiN compared to  $ZrO_2$  [25]. The estimated activity energies of  $ZrO_2$  and TiN in present SPSed composites were 124.1 and 203.1 kJ/mol respectively, as shown in Fig. 6. Also, the isolated TiN particles in the composite inhibited the growth of TiN grains.

The typical physical and mechanical properties of asobtained ZrO<sub>2</sub>-TiN composites are listed in Table 2. It is seen that except the ZT13 and ZT14 composites sintered at the pressure of 20 and 40 MPa all of the other composites reach the high relative densities above 99%. For all of the dense composites, the Vickers hardness was determined in a small range of 13.90-15.53 GPa and exceeded that of single phase zirconia (12 GPa) [26]. The reason is due to the reinforcement effect of TiN particles with the higher hardness of 18.3 GPa [27]. Also, the Young's moduli of composites were determined within a narrow range of 216.2-228.0 GPa, being insensitive to the ranged sintering parameters and confirming the microstructural homogeneity of composites. The measured modulus values are close to the theoretic value (226.5 GPa) calculated by the rule of mixture of TiN (465 GPa) and ZrO<sub>2</sub> (200 GPa) [28]. Additionally, the indentation fracture toughness of composites was evaluated. It is found that for the dense composites the toughness values spanned over a range of 2.91-5.44 MPa  $\cdot$  m<sup>1/2</sup>, and there is no obvious change tendency of fracture toughness as the function of sintering temperature, heating rate, annealing time, and applied pressure. The ZT02 composite shows the highest toughness of 5.44 MPa  $\cdot$  m<sup>1/2</sup> and the ZT16 composite has the lowest toughness of 2.91 MPa  $\cdot$  m<sup>1/2</sup>. It is



Fig. 6. Sintering dynamic curves of ZrO<sub>2</sub> and TiN nano particles in the composites.

supposed that the fracture toughness of composites is affected by the complex factors including the distribution of constitutive particle, grain size, residual stress, and phase transformation [29-33].

## Conclusions

Nano ZrO<sub>2</sub>-10 vol.% TiN composite was synthesized by spark plasma sintering using nano sized 3Y-ZrO<sub>2</sub> and TiN particles as the initial materials with the variable sintering parameters of temperature, holding time, heating rate, and pressure. In the densified composites, the main compositions were confirmed as t-ZrO<sub>2</sub> and c-TiN. It was found that the sintering temperature exceeding 1100 °C and the applied pressure above 60 MPa were the two key factors to achieve full densification of composites. The grain sizes of ZrO<sub>2</sub> and TiN were controlled below 243 and 171 nm, respectively. The Vickers hardness and Young's modulus were insensitive to the sintering parameters, showing a narrow range of 13.90-15.53 GPa and 216.2-228.0 GPa, respectively. Additionally, the fracture toughness spanned over a range of 2.91-5.44 MPa  $\cdot$  m<sup>1/2</sup> owing to the complex influences of particle distribution, residual stress, grain size, or phase transformation.

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