Nano ZrO₂–TiN composites with high strength and conductivity

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Nano ZrO₂–TiN (10–40 vol.%) composites were successfully fabricated by spark plasma sintering (SPS) at 1200°C under 80 MPa. The as-obtained composites remained nanosized grains of ZrO₂ and TiN below 200 nm. The physical and mechanical properties of composites were systemically investigated. It was found that above 20 vol.% TiN the composites were electrically conductive. 30 and 40 vol.% TiN reinforced composites possessed the highest flexural strength of 1459.7 MPa and maximum electrical conductivity of 17081.7 S·m^{−1} respectively.

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1. Introduction

ZrO₂ ceramic has been widely investigated due to its high strength, high fracture toughness, remarkable wear resistance, and excellent chemical corrosion resistance.^{1)–3)} To date, ZrO₂ based composites, including ZrO₂–Al₂O₃, ZrO₂–TiC, ZrO₂–TiN, ZrO₂–TiB₂, ZrO₂–BN, ZrO₂–Graphene, and ZrO₂–WC etc., have been fabricated and their remarkable physical and mechanical properties have been investigated.^{4)–11)} It is known that TiN has a high hardness of 17.2 GPa and low electrical resistivity of $2.5 \times 10^{-7} \Omega \cdot \text{m}$.^{12),13)} It is a good candidate to be a conductive and reinforcing phase in ZrO₂–TiN composites.^{14)–17)} For example, K. Vanmeensel et al. fabricated the ZrO₂–TiN composites (35–90 vol.% TiN) with good electrical conductivity of $2.22 \times 10^6 \text{ S} \cdot \text{m}^{-1}$ (90 vol.% TiN) and high fracture toughness of 7.6 MPa·m^{1/2} (35 vol.% TiN) using the pulsed electric current sintering method.¹⁴⁾ S. Salehi et al. prepared 1.75 mol % Y₂O₃–stabilized ZrO₂–TiN composites (35–95 vol.% TiN) densified by hot pressing and obtained the highest fracture toughness of 5.9 MPa·m^{1/2} and bending strength of 1674 MPa with 40 vol.% TiN.¹⁶⁾ Also, it has been confirmed that the Young's modulus and electrical conductivity of ZrO₂–TiN composites increased with the increment content of TiN.

In present work, in order to determine the electrically conductive criteria of TiN and the properties of composites with low loading TiN, ZrO₂–10, 20, 30, 40 vol.% TiN composites were designed. Nanosized ZrO₂ and TiN particles were used to prepare the composites by spark plasma sintering (SPS). Owing to the low temperature fast sintering and high pressure, spark plasma sintering was considered to be an effective technique to hinder grain growth and preserve the nano ZrO₂ and TiN grains.¹⁸⁾ The microstructure, physical and mechanical properties of SPSed composites were investigated compared to pure zirconia.

2. Experimental procedures

Commercial 3Y-ZrO₂ (27 nm, Tosoh Corp., Japan) and TiN (Purity, 99.2%) (20 nm, Hefei Kaier Nano Energy Tech Co., Ltd., China) particles were used as the initial materials. The selected volume content of TiN were 10, 20, 30, and 40%, labeled as Z10T, Z20T, Z30T, and Z40T respectively. The powders were weighed by an electronic scale with an accuracy of 10^{−3} g and then put into a zirconia jar and milled for 5 h at 300 rpm using zirconia balls as milling media in a planetary ball milling machine (PULVERISETTE 5, FRITSCH GmbH, Germany). Ethanol was used as dispersant. After drying in an oven at 70°C, the mixture was sieved through a 120 mesh sieve. The obtained mixture powder was poured into a graphite die with an inner diameter of 20 mm and sintered in vacuum (6 Pa) by a SPS machine (LABOX TM-315 SPS, Sinter Land Inc., Japan). A thin carbon foil (0.2 mm thickness) was interposed between the inner die wall and the punches for achieving the good electric and thermal contact, and the outer of die was wrapped by a carbon felt to limit the heat loss by radiation. Below 900°C the heating rate was kept at 50°C/min and above 900°C the heating rate was decreased to 10°C/min. When at 900°C, the applied pressure reached 80 MPa. The samples were densified at 1200°C for 20 min. The SPS processing parameters (temperature, shrinkage, pressure) were recorded during processing. Samples' cracking induced by thermal shock and internal stresses was prohibited by linearly decreasing the pressure while cooling down at a rate of 20°C/min. For comparison, pure zirconia was also sintered under the same condition, named as Z00T. After grinding off the graphite surface contaminations, the specimens were machined and polished down to 1.0 μm diamond grids. The density was measured by the Archimede's method. The phase compositions were examined by an X-ray diffraction (XRD) analyzer (RINT-2500, Rigaku Co., Japan) using Cu Kα radiation. The Vickers hardness was tested by a microhardness tester (MVK-E, Akashi Co., Japan) under a load of 9.8 N. The fracture toughness was evaluated by an indentation microfracture (IM) method by using a Vickers hardness tester (AVK-A, Akashi Co., Japan) to induce

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the diagonal cracks under a load of 49 N. Five indents and diagonal cracks were observed by a scanning electron microscope (SEM) (SU8010, HITACHI Corp., Japan). The polished surface of composites was thermally etched at 1000°C in vacuum (10^{-3} Pa) for 1 h and the mean grain sizes of ZrO_2 and TiN were measured by SEM image analysis. The flexural strength measurement was conducted by using a three-point bending mode in a universal testing machine (SHIMADZU AG-X PLUS AUTOGRAF, Tokyo, Japan) with a crosshead speed of 0.5 mm/min. The dimension of samples was $2 \times 2 \times 18 \text{ mm}^3$ and the span was 16 mm. The Young's modulus was determined by an ultrasonic equipment (TDS 3034B, Tektronix Inc., USA), and the electrical conductivity was measured using the four probe method.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of fabricated composites with different volume fraction of TiN. The detected phases in all of the samples (Z00T-Z40T) were t- ZrO_2 and TiN. No reaction between the phases and no other oxides deriving from oxidation of TiN particles were detected. The wide diffraction peaks of ZrO_2 and TiN confirmed the nano sized grains in the bulk composites.

Figures 2(a)–2(e) show the scanning electron microscope (SEM) micrographs of thermal etched surface of pure zirconia and ZrO_2 -TiN composites. The grain size distribution was narrow and the average grain size was below 200 nm. In the pure zirconia ceramic (Z00T), the average grain size was 169 nm [Fig. 2(a)]. In the composites of Z10T-Z40T, the mean grain sizes of ZrO_2 (light gray) were 151, 118, 129, 122 nm and those of TiN (dark gray) were 55, 74, 91, 87 nm respectively [Figs. 2(b)–2(e)]. The introduction of TiN has effectively inhibited the growth of ZrO_2 grains through the pinning effect. On the other hand, higher content of TiN enhanced their contact ratio so as to accelerate the growth of TiN grains. In Z10T and Z20T, the TiN grains were homogeneously distributed in the ZrO_2 matrix. Whereas in Z30T and Z40T, coalescence of TiN particles occurred. This is probably ascribed to the high volume fraction of TiN and the difficulty of achieving a complete particle deagglomeration by ball milling.

Figures 3(a)–3(d) show the SEM micrographs of fracture surface of Z00T and Z20T-Z40T. The pure zirconia Z00T shows

Fig. 1. X-ray diffraction (XRD) patterns of nano ZrO_2 -TiN composites: (a) Z00T, (b) Z10T, (c) Z20T, (d) Z30T, and (e) Z40T.

an intergranular fracture mode and the ZrO_2 grains in Z20T-Z40T present the mixed fracture of intergranular and transgranular modes. Mainly, the TiN particles exhibit the intergranular damage. The thermal expansion coefficient of TiN ($9.4 \times 10^{-6}/\text{K}$) is lower than that of 3Y- ZrO_2 ($10.8 \times 10^{-6}/\text{K}$),¹⁹⁾ which means that tensile stresses exist at the interfaces between TiN and ZrO_2 particles and the cracks would be prone to deflect along the grain boundaries between TiN and ZrO_2 grains.

Table 1 lists the measured physical and mechanical properties of ZrO_2 -TiN composites. It is seen that when the content of TiN was increased up to 20 vol.% the ceramic became electrically conductive. The electrical conductivity of Z20T was $308.6 \text{ S}\cdot\text{m}^{-1}$. With the progressive increase of TiN loading, the electrical conductivities of composites were further increased up to 2727.4 and $17081.7 \text{ S}\cdot\text{m}^{-1}$ respectively (Z30T and Z40T). It means that the introduction of TiN particles above a percolation threshold could effectively provide a conductive network for the electrons. The Vickers hardness of composites initially increased

Fig. 2. Scanning electron microscope (SEM) micrographs of thermal etched surface of nano ZrO_2 -TiN composites: (a) Z00T, (b) Z10T, (c) Z20T, (d) Z30T, and (e) Z40T.

Fig. 3. SEM micrographs of fracture surface of nano ZrO_2 -TiN composites: (a) Z00T, (b) Z20T, (c) Z30T, and (d) Z40T.

Table 1. Measured physical and mechanical properties of nano ZrO₂-TiN composites

Samples	Relative density (%)	Mean grain size (nm)	Electrical conductivity (S·m ⁻¹)	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa·m ^{1/2})	Young's modulus (GPa)
Z00T	100	ZrO ₂ : 169	—	13.9 ± 0.2	1987.1 ± 134.6	2.68 ± 0.03	214.0
Z10T	98.8	ZrO ₂ : 151 TiN: 55	—	14.3 ± 0.4	1360.2 ± 117.4	3.35 ± 0.06	203.5
Z20T	99.5	ZrO ₂ : 118 TiN: 74	308.6 ± 2.3	15.4 ± 0.5	1339.0 ± 118.8	3.57 ± 0.22	228.6
Z30T	99.1	ZrO ₂ : 129 TiN: 91	2727.4 ± 9.4	14.7 ± 0.4	1459.7 ± 98.2	3.44 ± 0.05	233.4
Z40T	98.7	ZrO ₂ : 122 TiN: 87	17081.7 ± 36.4	14.2 ± 0.3	1308.0 ± 42.9	3.46 ± 0.11	242.2

Fig. 4. SEM micrographs of crack propagation generated by a Vickers indentation on the polished surface of nano ZrO₂-TiN composites.

from 13.9 to 15.4 GPa with the increasing TiN content up to 20 vol.% and then decreased down to 14.2 GPa for the Z40T sample. Compared to the Z00T sample, the progressive enhancement of hardness of Z10T and Z20T composites is possibly due to the higher hardness of TiN (17.2 GPa), and the decrease of hardness for higher TiN loading (Z30T and Z40T) is probably ascribed to the grain growth of TiN particles and the existence of residual porosity. The flexural strength of pure zirconia was 1987.1 MPa, and those of composites were also high as 1308.0–1459.7 MPa. Nano composite containing 30 vol.% TiN resulted in the highest flexural strength. In comparison with pure zirconia, the decrease of strength of composites was possibly associated with the residual pores presented by the relative densities as well as the inner tensile stresses. The fracture toughness of composites was in the range of 3.35–3.57 MPa·m^{1/2} and it was significantly higher than that of pure zirconia (2.68 MPa·m^{1/2}). **Figure 4** shows the crack propagation generated by the Vickers indentation under the load of 49 N. The TiN grains could effectively promote crack deflection at the grain boundaries, enhancing the fracture toughness. By increasing the TiN loading, the Young's modulus of composites showed a general tendency of increase, which was due to the significantly higher Young's modulus of TiN (465 GPa).¹²⁾ The elastic modulus of Z40T was the highest as 242.2 GPa.

4. Conclusions

Nano 10–40 vol.% TiN reinforced ZrO₂ composites were successfully fabricated by SPS at 1200°C under 80 MPa. The introduction of TiN effectively contributed to the grain refinement of zirconia. Above 20 vol.% TiN, the composites became electrically conductive. The maximum electrical conductivity of 17081.7 S·m⁻¹ and the highest flexural strength of 1459.7 MPa were obtained from the composites containing 40 and 30 vol.% TiN respectively. The Vickers hardness of composites initially increased from 13.9 to 15.4 GPa with the increasing TiN content up to 20 vol.% and then decreased down to 14.2 GPa (40 vol.% TiN). The fracture toughness of composites was in the range of 3.35–3.57 MPa·m^{1/2}. The elastic modulus of composites generally increased with the increment of TiN and 40 vol.% TiN reinforced composite showed the highest value of 242.2 GPa.

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