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ZrO_2–WC nanocomposites with superior properties

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Abstract

Fully dense ZrO_2-based nanocomposites with 5–40 vol.% WC were produced by hot pressing at 1450 °C for 1 h. The hardness and bending strength of the composites increases with increasing WC content, whereas the toughness hardly changes. An exceptionally high strength of 2 GPa combined with a hardness of 14.80 GPa and an excellent fracture toughness of 9.4 MPa $m^{1/2}$ was obtained for the 2 mol% Y_2O_3 stabilised ZrO_2-based composite with 40 vol.% WC. Such an attractive combination of properties is quite unique for a ceramic composite and is only matched by WC–Co cermets. The composites are substantially harder and stronger than the fine-grained Y-TZP, whereas the excellent toughness of Y-TZP is maintained. The strength improvement was accompanied with a change in fracture mode of the ZrO_2 grains from intergranular to transgranular. The ZrO_2–WC nanocomposites were found to slightly plastically deform before fracturing during bending.

Keywords: Nanocomposites; Mechanical properties; Strength; ZrO_2–WC

1. Introduction

ZrO_2-based ceramics have been demonstrated to be the strongest and toughest oxide yet produced.[1] The excellent properties are attributed to the stress-induced phase transformation from tetragonal to monoclinic ZrO_2. The modest hardness however limits their use in some advanced tribological applications. The addition of a secondary hard phase could increase the hardness, while maintaining the high toughness due to transformation toughening and crack deflection. ZrO_2-based composites such as ZrO_2–TiB_2, ZrO_2–TiCN, ZrO_2–TiN, ZrO_2–TiC have recently received large attention.[2] ZrO_2–WC composites have also been investigated and show promising properties.[3,4] The toughness of yttria-stabilized zirconia (Y-TZP) based composites with a WC nanometer sized starting powder content up to 50 vol.% could be optimised by judicious adjustment of the overall yttria content by mixing monoclinic and 3 mol% Y_2O_3 co-precipitated ZrO_2 starting powders. An optimum fracture toughness of 9 MPa $m^{1/2}$ was obtained for a 40% WC composite with an overall yttria content of 2 mol%.[4] Moreover, the hardness, strength as well as fracture toughness of the ultra fine grained composites with a nanometer sized WC source was significantly higher than with micrometer sized WC.[4] Transformation toughening was found to be the major toughening mechanism in ZrO_2–WC composites with up to 30 vol.% WC, whereas the contribution of crack deflection and bridging is significant at a secondary phase content above 30 vol.%.[4] The addition of micrometer-sized WC grains to a ZrO_2 matrix was also reported to increase the hardness significantly, although the reported toughness values were rather low.[3,5,6] The major toughening mechanisms in the ZrO_2–WC composites investigated were identified to be microcracking, crack bridging, crack deflection and crack branching.[7] The coherent ZrO_2/WC interface[3] indicates a good bonding between the two phases, what could improve the mechanical properties.

To explore the potential of the ZrO_2–WC composite system, nanocomposites were prepared and investigated.

2. Experimental procedure

The starting powders used to fabricate the ZrO_2–WC composites are listed in Table 1. The MBN grade J550 WC nanopowder is obtained by mechanical milling. According to the supplier's data, the D_{50} of the powder is 2 μm. The individual WC crystal size is 18 nm, as measured by X-ray diffraction line broadening. The Y_2O_3 stabiliser content of the ZrO_2 matrix was fixed at 2 mol%, based on the previous[4] reported results, by mixing pure ZrO_2 powder (Tosoh grade TZ-0, Japan) and a 3 mol% Y_2O_3 co-precipitated ZrO_2 powder (Daiichi grade HSY-3U, Japan) in the appropriate ratio. Multidirectional mixing (Turbula) in ethanol using WC/Co milling balls was per-

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Table 1
Starting powers used to manufacture ZrO_2–WC composites

Powder	Supplier	Grade	Powder size	Composition
ZrO_2	Daiichi	HSY-3U	30 nm	3 mol% Y_2O_3
ZrO_2	Tosoh	TZ-0	27 nm	Pure ZrO_2
WC	MBN	J550	Agglomerates <10 μm	WC crystal size 18 nm
WC	Eurotungstène	CW5000	1.0 μm	–
Al_2O_3	Baikowski	SM8	0.6 μm	–

formed for 48 h. After cold pre-compression at 30 MPa, the samples were hot pressed (W 100/150-2200-50 LAX, FCT, Rauenstein, Germany) in vacuum for 1 h at 1450, 1550 or 1650 °C under a mechanical load of 28 MPa, with a heating rate of 50 °C/min and a cooling rate of 10 °C/min. The samples were separated from the furnace atmosphere by the graphite hot press set-up, whereas the sliding contacts were sealed by boron nitride.

Microstructural investigations were performed by scanning electron microscopy (SEM, XL 30 FEG, FEI, Eindhoven, The Netherlands). X-ray diffraction analysis was conducted on a θ–θ diffractometer (3003-TT, Seifert, Ahrensburg, Germany) using Cu Kα radiation (40 kV, 30 mA).

The elastic modulus, E, of the ceramic specimens was measured by the resonance frequency method,[8] measured on a Grindo-sonic (J.W. Lemmens, Elektronika N.V. Leuven, Belgium). The Vickers hardness, HV_{10}, was measured on a Zwick hardness tester (Model 3202, Zwick, Ulm, Germany) with a load of 10 kg. The fracture toughness was obtained by the Vickers indentation technique, based on crack length measurements of the radial crack pattern produced by HV_{10} indentations. The K_{IC} values were calculated according to the formula of Anstis.[9] The flexural strength at room temperature was measured in a three-point bending test. The test specimens (25.0 mm × 4.7 mm × 1.7 mm) were machined out of the hot pressed disc. All surfaces were ground with a Diamond Board MD40 75 B55 grinding wheel. The span width was 20 mm with a crosshead displacement of 0.1 mm/min.

3. Results and discussion

The microstructures of the ZrO_2–WC composites with 5, 10, 20 and 40 vol.% WC are presented in Fig. 1. The bright phase is WC, whereas the dark phase is ZrO_2. The WC phase is homogeneously distributed in the composites indicating that the powder mixing was good. The individual WC particles however are mainly present as small agglomerates in the composites. Close observation reveals that a significant amount

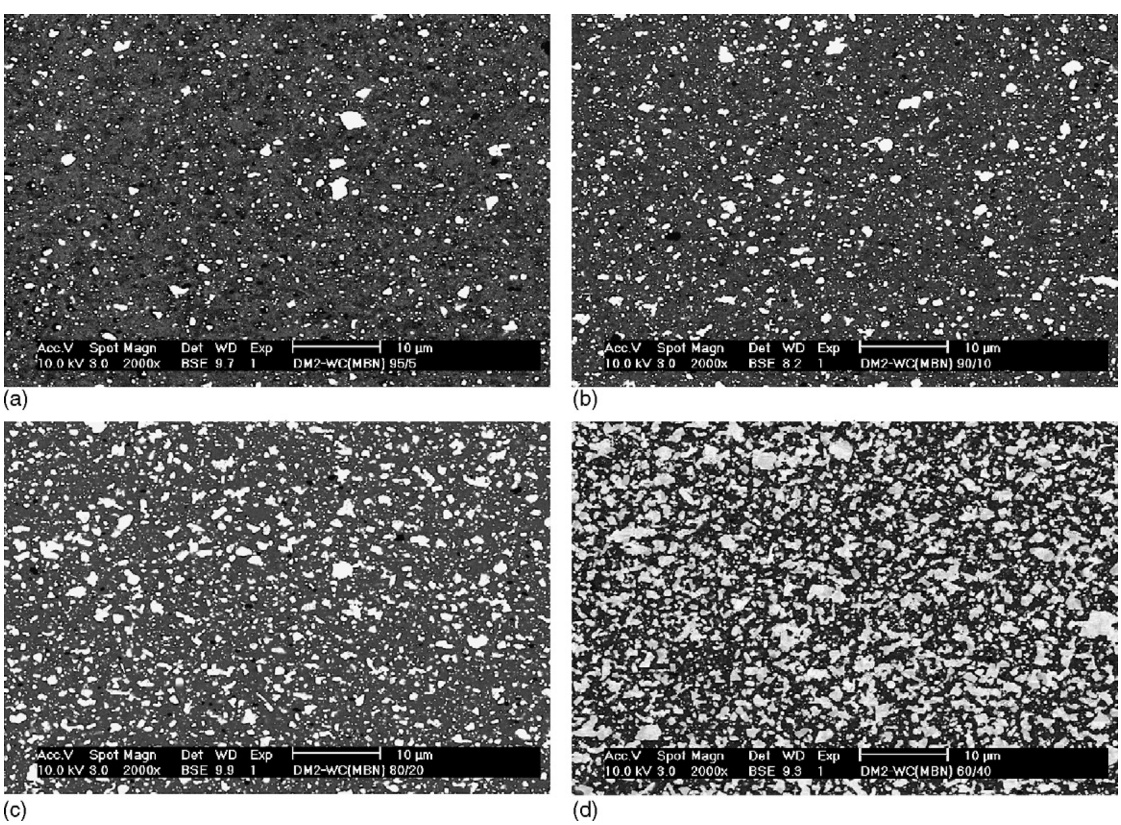

Fig. 1. Microstructure of ZrO_2 based composites with 5 (a), 10 (b), 20 (c) and 40 (d) vol.% of WC (MBN grade). The white phase is WC, the dark phase is ZrO_2.

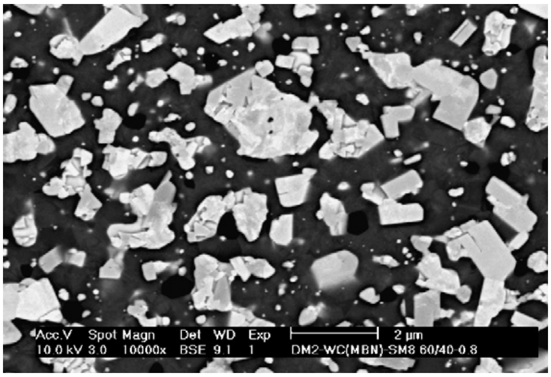

Fig. 2. Microstructure of a ZrO_2-based composite with 40 vol.% WC, showing the existence of bright WC nanoparticles in a darker ZrO_2 matrix.

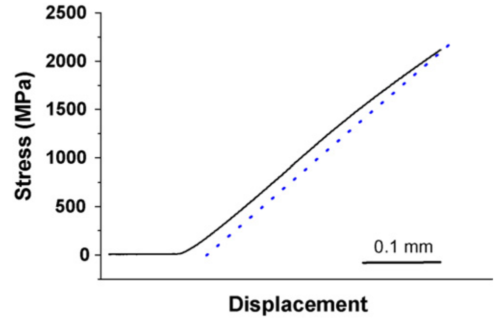

Fig. 3. 3-point bending response of the ZrO_2 nanocomposite with 40 vol.%WC.

of individual separated nanoparticles are dispersed in the ZrO_2 matrix, as shown in Fig. 2.

The properties of the composites are summarized in Table 2. Compared to the pure ZrO_2 material, the *E*-modulus, hardness and strength of the composites is substantially higher. Although the toughness of the composites is lower, an excellent value of 9.0 MPa $m^{1/2}$ was obtained. The hardness of the ZrO_2–WC powder based composites increases from 12.24 GPa for the 5 vol.% WC composite up to 14.80 GPa for the 40 vol.% WC composite, whereas the flexural strength also increases significantly from about 1500 up to 2000 MPa. The excellent toughness on the other hand hardly changes with the addition of 5 up to 40 vol.% WC. The composite with 40 vol.% WC has an exceptional combination of hardness (14.80 GPa), flexural strength (2.0 GPa) and fracture toughness (9.4 MPa $m^{1/2}$). Such excellent properties are unique for ceramics, and can only be matched my WC–Co cermets.

The addition of a small amount of alumina powder is reported to increase the fracture toughness of co-precipitated powder based Y-TZP ceramics.[10] The fracture toughness of sintered ceramics, obtained from mechanically mixed Al_2O_3/co-precipitated Y-TZP as well as powder from co-precipitated Zr^{4+}, Y^{3+} and Al^{3+} mixtures, had an optimum fracture toughness at an alumina content of 5 vol.%.[11] Moreover, enhanced strength, fracture toughness and hardness were achieved by the addition of 10 vol.% alumina powder to co-precipitated 3 mol% Y-TZP materials.[12] The fracture toughness of Al_2O_3/Y_2O_3-coated powder based TZP ceramics can be tailored by selection of the overall Y_2O_3 content. A maximum toughness for Y-TZP with 2 wt.% alumina was obtained with an yttria content of 1.75 mol%. The optimum toughness of Al_2O_3/Y_2O_3-coated based Y-TZP was achieved at a hot pressing temperature of 1450 °C. The fracture toughness of the yttria-coated powder based TZP ceramics could be optimised by the addition of 2 wt.% Al_2O_3.[13]

The addition of 0.8 wt.% Al_2O_3 to the 40 vol.% WC composite, hot pressed at 1450 °C, slightly decreases the E-modulus and toughness but increases the hardness, whereas the strength remains high (see material grade 60/40-0.8 in Table 2).

The influence of the hot-pressing temperature was found to have a strong effect on the mechanical properties of the 40 vol.% WC composites with 0.8 wt.% Al_2O_3 addition. The hardness slightly decreases together with the density with increasing hot pressing temperature. This is mainly due to an increased monoclinic ZrO_2 content due to spontaneous transformation of tetragonal into monoclinic ZrO_2 during cooling from the hot pressing temperature, as indicated by XRD results. It should however be clear that the ZrO_2 phase in all ceramics hot pressed at 1450 °C was fully tetragonal. The fracture toughness also decreases with increasing sintering temperature, due to a reduced transformability of the t-ZrO_2 phase, which already partially spontaneously transformed. The strength however was found to decrease substantially when the hot pressing temperature was increased from 1450 up to 1650 °C. The significant decrease in strength after hot pressing at 1650 °C indicates that some excessively large WC grains might be formed that act as crack origin.

The nanopowder based ZrO_2–WC–Al_2O_3 (60/40-0.8) and ZrO_2–WC (60/40) composites have a comparable hardness, a comparable or higher fracture toughness, and a superior strength

Table 2
Properties of ZrO_2–WC composites

Material grade	Temperature (°C)	WC (Vol.%)	*E* (GPa)	HV_{10} (GPa)	K_{IC} (MPa $m^{1/2}$)	Flexural strength (MPa)	Density (g/cm^3)
ZrO_2	1450	0	203 ± 1	11.95 ± 0.01	10.1 ± 0.1	1257 ± 114	6.06
95/5	1450	5	226 ± 1	12.24 ± 0.02	9.2 ± 0.3	1532 ± 148	6.56
91/10	1450	10	238 ± 1	12.56 ± 0.04	9.0 ± 0.4	1731 ± 52	7.05
80/20	1450	20	271 ± 3	13.38 ± 0.09	9.2 ± 0.3	1704 ± 81	8.04
60/40	1450	40	336 ± 1	14.80 ± 0.14	9.4 ± 0.6	2010 ± 97	9.93
60/40-0.8[a]	1450	40	328 ± 2	15.24 ± 0.08	8.5 ± 0.4	1964 ± 88	9.80
60/40-0.8[a]	1550	40	345 ± 2	14.75 ± 0.09	8.6 ± 0.2	1743 ± 36	9.77
60/40-0.8[a]	1650	40	347 ± 2	14.25 ± 0.03	7.3 ± 0.2	1013 ± 663	9.73
CW5000-0.8[a]	1450	40	340 ± 2	15.08 ± 0.03	8.5 ± 0.2	1255 ± 65	9.79

[a] With 0.8 wt.% Al_2O_3 addition.

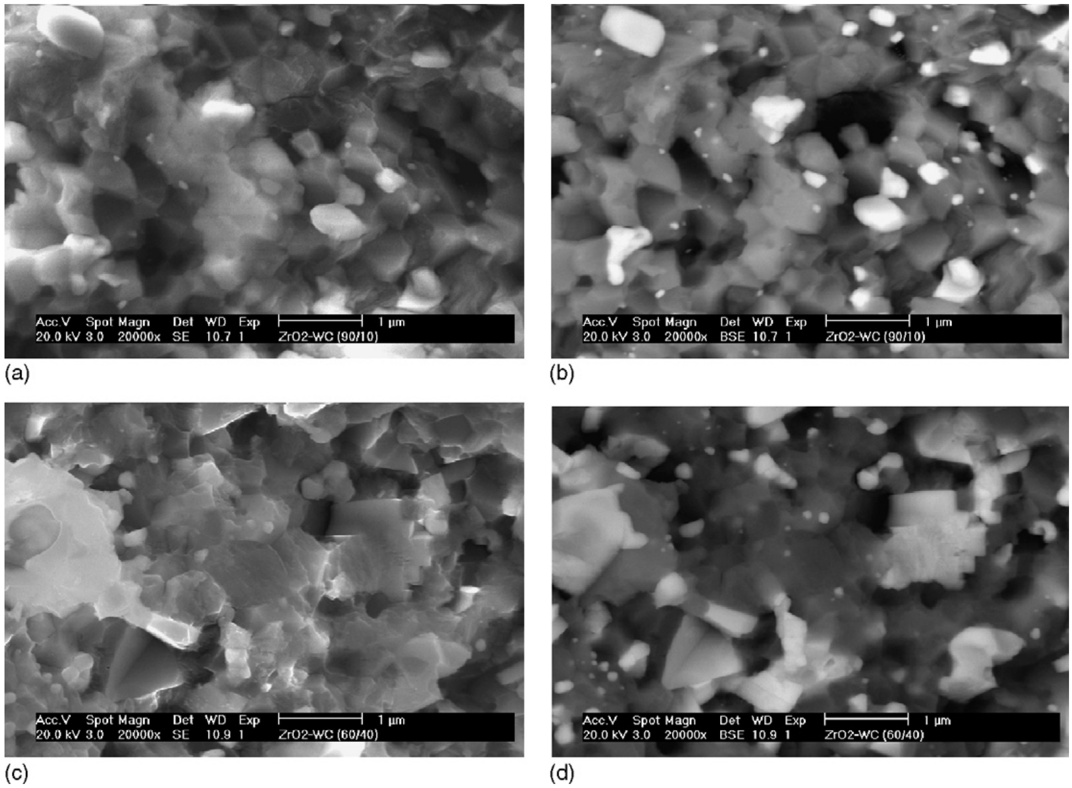

Fig. 4. Secondary (a and c) and backscattered (b and d) electron contrast micrographs of the fracture morphology of a ZrO_2-composite with 10 (a and b) and 40 (c and d) vol.% WC. The WC phase is white in backscattered electron contrast.

compared to the micrometer WC powder based (CW5000 grade) composite with Al_2O_3 addition, as summarised in Table 2.

A strength improvement by the incorporation of nanoparticles in ceramics has been realized in Al_2O_3 and Si_3N_4 based composites.[7,8] However, the strengthening mechanism still remains unclear. Therefore, the stress–displacement curve of the ZrO_2–WC (60/40) composite was examined, as presented in Fig. 3. Surprisingly, the linear elastic stage is followed by a non-linear behaviour, indicating that the composite is slightly plastic before fracturing. We believe this mechanical behaviour is closely related to the exceptionally high strength. However, this behaviour is not observed in the fine-grained ZrO_2 and composites with micrometer sized WC. This implies that WC nanoparticles exert a big influence on the mechanical behaviour.

The fracture morphology of the composites was examined, revealing that the fracture mode of the ZrO_2 grains changes from intergranular to transgranular with increasing WC content, as shown in Fig. 4, indicating that grain boundary bonding becomes stronger with increasing WC content. This observation is in agreement with that reported for Al_2O_3–SiC nanocomposites.[14,15]

4. Conclusions

Fully dense ZrO_2-based nanocomposites with 5 up to 40 vol.% WC were produced by hot-pressing at 1450 °C for 1 h. The strength was found to decrease drastically at higher hot-pressing temperatures.

The ZrO_2–WC composites are substantially harder and stronger than the fine-grained Y-TZP, whereas the excellent toughness of Y-TZP is maintained. The hardness and bending strength of the composites increases, whereas the toughness hardly changes with increasing WC content.

An exceptionally high strength of 2 GPa combined with a hardness of 14.80 GPa and an excellent fracture toughness of 9.4 MPa $m^{1/2}$ was obtained for the 2 mol.% Y_2O_3 stabilised ZrO_2-based composite with 40 vol.% WC hot-pressed at 1450 °C. Such an attractive combination of properties is quite unique for a ceramic composite and is only matched by WC–Co cermets.

The strength improvement, compared to that of the ZrO_2 monolith, was accompanied with a change in fracture mode of the ZrO_2 grains from intergranular to transgranular. The ZrO_2–WC nanocomposites were found to slightly plastically deform before fracturing during bending.

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