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Development of ZrO_2–WC composites by pulsed electric current sintering

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Abstract

ZrO_2–WC ceramic composites with 40 vol% WC were consolidated by pulsed electric current sintering (PECS) for 4 min at 1450 °C under a pressure of 60 MPa. The effect of ZrO_2 stabilizers and the source of WC powder on the densification, phase constitution, microstructure and mechanical properties of the ZrO_2–WC composites were investigated and analyzed. The experimental results revealed that the amount and type of ZrO_2 stabilizers played a primary role on the phase constitution and mechanical properties of the composites in comparison to the morphology and size of the WC powder. The 2 mol% Y_2O_3-stabilized composites exhibited much better mechanical properties than that of 1.75 mol% Y_2O_3-stabilized or 1 mol% $Y_2O_3 + 6$ or 8 mol% CeO_2 co-stabilized composites. A Vickers hardness of 16.2 GPa, fracture toughness of 6.9 MPa m$^{1/2}$, and flexural strength of 1982 MPa were obtained for the composites PECS from a mixture of nanometer sized WC and 2 mol% Y_2O_3-stabilized ZrO_2 powder.

Keywords: ZrO_2; Carbides; Composites; SPS; Mechanical properties

1. Introduction

Tetragonal ZrO_2 polycrystals (TZP) are usually doped with Y_2O_3, CeO_2, CaO or other oxides to stabilize the high temperature tetragonal phase at room temperature. The transformation of tetragonal (t) to monoclinic (m) ZrO_2 phase contributes to the excellent mechanical properties such as high fracture toughness and bending strength. The application of structural ZrO_2 ceramics can be broadened by the incorporation of hard carbide inclusions in the TZP matrix, such as in TZP–SiC,[1,2] TZP–TiC[3] and TZP–WC[4–9] composites. Y_2O_3-stabilized TZP with WC addition was systematically investigated from the aspects of composition determination and sintering control.[6] Excellent combinations of hardness, fracture toughness and bending strength were obtained in hot pressed ZrO_2–40 vol% WC composites, which may partially replace the traditional WC–Co cemented carbides for some specific applications.[6,7]

In ZrO_2–WC composites, the mechanical properties can be modified both by the properties of WC and the ZrO_2 phases. A much higher hardness was obtained for composites with finer WC inclusions in comparison with coarse WC grains, even though the finer WC grades were more difficult to densify by hot pressing, and the fracture toughness of the composites is generally higher than for monolithic ZrO_2 ceramics.[6,7] In monolithic TZP materials, the t- to m-ZrO_2 phase transformation is a dominant toughening mechanism. The type and amount of stabilizers in ZrO_2 have a great impact on toughness. It can therefore be expected that the toughness of ZrO_2–WC composites can be manipulated by changing the type and amount of ZrO_2 stabilizers. Moreover, it has been reported that the hydrothermal stability and fracture toughness of Y–TZP can be improved by CeO_2 doping.[10,11] For hot pressed 2 mol% Y_2O_3-stabilized Y–TZP composites with up to 50 vol% WC addition, the best combination of toughness, hardness and strength was reported for ZrO_2 composites with 40 vol% WC addition.[6,7] For $Y_2O_3 + CeO_2$ co-stabilized ZrO_2 ((Y,Ce)–TZP), the optimum toughness was obtained with 1.0–1.5 mol% Y_2O_3 + 6–8 mol% CeO_2.[10,11]

The present study aimed to investigate the possibility to densify ZrO_2–WC composites by means of a very fast sintering technique, i.e. pulsed electric current sintering (PECS), which is also known as spark plasma sintering (SPS). The influence of

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Table 1
Starting powers used to make ZrO_2–40 vol% WC composites

Powder	Supplier	Grade	Powder size[*]
WC	MBN	J550	Agglomerates <10 μm; crystals <30 nm (XRD)
WC	ZhangYuan (ZY)	–	50 nm (XRD)
WC	OMG	Jet-milled	0.2 μm
WC	Eurotungstène	CW5000	0.8–1.0 μm
ZrO_2	Tosoh	TZ-0	27 nm
ZrO_2	Tosoh	TZ-3Y	30 nm
Y_2O_3	Atlantic Equipment Engineers	YT-603	–
$Ce(NO_3)_3 \cdot 6H_2O$	Aldrich Chemical company	–	–
Al_2O_3	Baikowski	SM8	0.8–1.0 μm

[*] Supplier data.

the size and morphology of the WC starting powder and the type and amount of ZrO_2 stabilizers on the mechanical properties of ZrO_2 composites with 40 vol% WC addition was investigated.

2. Experimental procedure

2.1. Materials preparation

ZrO_2–WC composites were prepared from three grades of nanometer sized and 1 μm sized WC powders with different morphologies and degree of agglomeration. The ZrO_2 matrix was stabilized with 1 mol% Y_2O_3 + 6 or 8 mol% CeO_2 (1Y6Ce or 1Y8Ce) prepared according to the powder coating technique.[11,12] Additionally, 1.75 and 2 mol% Y_2O_3-stabilized ZrO_2 (TM1.75 and TM2) were prepared by mixing commercial available 3Y–ZrO_2 and m-ZrO_2 powders. Additionally, 0.75 wt% Al_2O_3 was added to the ZrO_2–WC powder mixtures to assist sintering and limit ZrO_2 grain growth. Information on the starting powders is provided in Table 1.

To simplify the description, the composite grades are labelled as C1–C7, as listed in Table 2. The C1–C4 grades represent the composites composed of the nanometer sized MBN WC powder and the 1Y6Ce, 1Y8Ce, TM1.75 and TM2 ZrO_2 grades, which were selected to investigate the influence of the ZrO_2 composition on the composite properties. The composition of the ZrO_2 matrix was fixed to TM2, whereas the WC source was changed to ZY, OMG and CW5000 for the composite grade C5, C6 and C7 respectively. The powders were mixed in ethanol for 48 h on a multidirectional mixer (Turbula type) using WC–Co milling balls. The suspension was dried in a rotating evaporator at 80 °C.

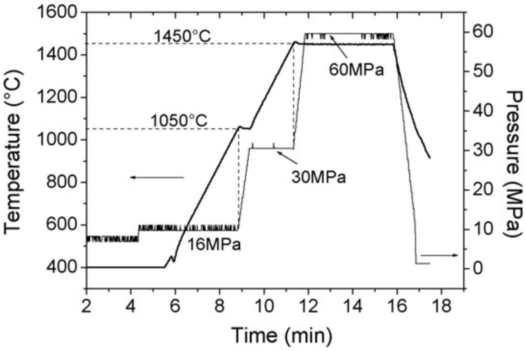

Fig. 1. PECS thermal and mechanical loading cycles to consolidate the ZrO_2–WC composites.

PECS (Type HP D 25/1, FCT Systeme, Rauenstein, Germany) was performed in a vacuum of 4 Pa. A pulsed electric current was applied with a pulse duration of 10 ms and pause time of 5 ms throughout all the experiments. The powder mixture (28.2 g) was poured into a cylindrical graphite die with an inner diameter of 30 mm and outer diameter of 66 mm and sintered for 4 min at 1450 °C under a maximum pressure of 60 MPa, with a heating and initial cooling rate of 200 °C/min. The thermal and mechanical loading cycles are shown in Fig. 1, in which the pressure was increased within 0.5 min from 16 to 30 MPa at 1050 °C, and adjusted within 0.5 min at 1450 °C from 30 to 60 MPa. Graphite paper was used to separate the

Table 2
Properties of the ZrO_2–40 vol% WC composites sintered at 1450 °C under a pressure of 60 MPa for 4 min

Grades	ZrO_2	WC	ρ (g/cm^3)	m/(m + t)[a] (vol%)	Δm[b] (vol%)	E (GPa)	HV$_{10}$ (GPa)	K$_{IC}$ (MPa.m$^{1/2}$)	TRS (MPa)
C1	1Y6Ce	MBN	9.75	32.2	32.1	369	14.9 ± 0.2	6.5 ± 0.1	816 ± 96
C2	1Y8Ce	MBN	9.80	40.7	20.0	369	14.7 ± 0.1	6.3 ± 0.2	884 ± 139
C3	TM1.75	MBN	9.66	42.3	22.2	378	14.4 ± 0.2	6.4 ± 0.2	1248 ± 57
C4	TM2	MBN	9.78	6.2	43.7	372	16.2 ± 0.1	7.3 ± 0.1	1873 ± 90
C5	TM2	ZY	9.76	6.1	47.6	360	16.0 ± 0.2	6.2 ± 0.1	1842 ± 70
C6	TM2	OMG	9.75	3.9	52.6	376	16.2 ± 0.2	7.0 ± 0.2	1982 ± 88
C7	TM2	CW5000	9.75	4.1	50.4	379	15.8 ± 0.1	7.3 ± 0.4	1914 ± 85
[c]ZrO_2	TM2	–	5.98	1.7	63.4	210	11.8 ± 0.1	6.5 ± 0.1	–

[a] Monoclinic ZrO_2 content.

[b] Δm: transformability of t-ZrO_2 phase.

[c] ZrO_2 obtained by PECS at 1450 °C for 2 min.