Journal of the European Ceramic Society **5** (1998) 1939–1943

PII: S0955-2219(98)00133-2
0955-2219/98/$—see front matter

The TZP–Chromium Oxide and Chromium Carbide Composites

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Abstract

Microstructure and mechanical properties of the 2·9(Y)TZP matrix composites with chromium carbide and chromium oxide inclusions were investigated. Two chromium carbides were used, Cr_3C_2 and Cr_7C_3. The TZP matrix powder was prepared by the coprecipitation-calcination technique. Attrition mixing allowed to homogenise the matrix and the additive powders. Coprecipitation was additionally applied in the case of the TZP–Cr_2O_3 system. Hot pressing at 1400°C for 40 min resulted in the higher densification than the pressureless sintering at 1500°C for 120 min. The TZP–carbide systems showed better properties and higher densification in the case of the Cr_7C_3 additive. It was related to the reaction between the matrix and Cr_3C_2. Microscopic observations revealed quite different crack propagation path in the system with the oxide and carbide additives. It allowed to suggest mechanisms of the toughness increase over the value of the pure matrix.

1 Introduction

Hard inclusions (WC, SiC, TiC, TiN, TiCN, TiB_2, Cr_2O_3) incorporated into the tetragonal zirconia polycrystalline matrix (TZP) increase hardness, fracture toughness, Young's modulus and wear resistance of the material[1–4]. The problems encountered in some of such materials are related to the possible reaction between the material constituents and the coefficient of thermal expansion (CTE) mismatch. The chemical reaction can change the starting composition of the system. This phenomenon occurs in the TZP-WC [2] and TZP-SiC[5] systems. The TEC mismatch can generate stresses in a system affecting its mechanical properties.

The present work extends the idea of such composites to the system of the TZP–chromium carbides. Very low difference of the CTE within this system ($11{\cdot}0\times10^{-6}$ °C^{-1} for TZP, $10{\cdot}3\times10^{-6}$ °C^{-1} for Cr_3C_2 and $10{\cdot}0\times10^{-6}$ °C^{-1} for Cr_7C_3) seems to be its advantage. Also the TZP–Cr_2O_3 system was included in the present investigations.

2 Experimental

Zirconia solid solution containing 2·9 mol% Y_2O_3 was applied. The powder was obtained by the coprecipitation–calcination technique.[6] The two chromium carbides, Cr_3C_2 and Cr_7C_3 were prepared by the self heating synthesis (SHS) method [7] using the relative elements as the starting materials. The carbides were attrition milled with the 2 mm TZP balls. Homogenisation of the powder mixtures was achieved by the 45 min attrition mixing of the relative powder mixture in ethyl alcohol.

In the case of the chromia additives the two procedures were applied. The one analogous to the indicated above and the second based on the hydroxide coprecipitation with the ammonia solution from the $ZrOCl_2$ and $Cr(NO_3)_3$ water solution. The hydroxide mixture was calcined at 1050°C for 45 min. Then the powder was attrition milled.

Densification of the materials was performed by the pressureless sintering and hot-pressing. Samples for the pressureless sintering were isostatically pressed under 250 MPa and fired in argon atmosphere at 1500°C for 120 min. The specimens with Cr_2O_3 additives were placed in the buffer mixture of equimolar mixture of Cr_2O_3 and Cr to avoid oxidation of the chromia particles in the composite.[8] The samples with the carbide additives were placed in a carbon bed. Hot-pressing was performed in one inch graphite mould at 1400°C

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under 25 MPa for 40 min. Again argon atmosphere was applied.

Densities of the samples were determined by the hydrostatic weighing. Their relative densities were estimated assuming the TZP, Cr_3C_2, Cr_7C_3 and Cr_2O_3 densities of 6·1, 6·54, 6·85 and 5·21 g cm^{-3}, respectively.

Vickers hardness was measured under 1·96 N load. Indentations for fracture toughness measurements were made under 49·05 N load. Palmqvist's crack model and Niihara equation[9] were applied. Elastic properties (Young's modulus) were determined by the ultrasonic measurements.[10]

3 Results and Discussion

3.1 The TZP–Carbide Systems

Phase composition of the pressureless sintered samples containing Cr_3C_2 and Cr_7C_3 are shown in the X-ray diffraction patterns (Fig. 1). The pattern A demonstrates the presence of Cr_7C_3 in the material having Cr_3C_2 as the only additive in the starting composition. Most probably this is due to the reaction of Cr_3C_2 with zirconia according to the eqn (1).

$$ZrO_2 + 7Cr_3C_2 = ZrC + 3Cr_7C_3 + 2CO + 2C \quad (1)$$

According to the thermodynamic calculations this reaction is possible under the applied sintering conditions.[11] It is worth noticing that no ZrC could be detected, but from our previous work[2] it happens that even low CO partial pressure (0·054 atm and 0·20 atm at 1400°C and 1500°C, respectively) stops the ZrC synthesis. Plausibly the local CO partial pressure due to the reaction surpasses the indicated levels. As should be expected no phase changes occured in the material with the Cr_7C_3 additive (Fig. 1B).

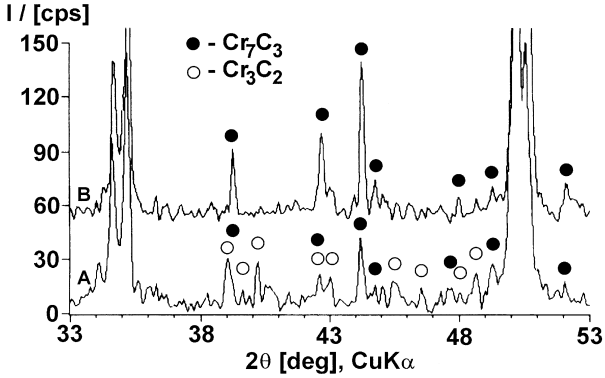

Fig. 1. X-ray diffraction patterns of the pressureless sintered composites containing in the starting composition 20 vol% Cr_3C_2—A and 20 vol% Cr_7C_3—B.

Sample densities, Young's modulus, hardness and fracture toughness of the TZP / carbide systems pressureless sintered and hot-pressed are shown in Table 2. Essentially lower densification and consequently poor properties result from the pressureless sintering.

Densification of the hot-pressed systems is generally high except of the Cr_3C_2 containing composites. The carbide additives lead to the increased elastic properties and hardness of the materials. Significant improvement of the fracture toughness of the composites is observed in the TZP/Cr_7C_3 system.

Crack deflection at the matrix/carbide (Cr_7C_3) interface is evident from the SEM micrograph in Fig. 2. This phenomenon seems to be the source of the observed fracture toughness increase. The TEM micrographs reveal the tight adherence of the matrix and carbide (Cr_7C_3) inclusions. An example is given in Fig. 3.

3.2 The TZP–oxide system

No reaction occurs in the system, as corroborated by the X-ray diffraction. Properties of the pressureless sintered and hot-pressed samples are given in Table 3.

Again, much lower densification occurs in the pressureless sintered bodies. They have lower Young modulus and hardness. In the hot-pressed samples an effective increase of these properties and fracture toughness compared to the pure matrix material occurs. It can be noticed that the Vickers hardness of these materials is higher than the corresponding ones having chromium carbide additives.

Figure 4 reveals the Cr_2O_3 grains spread within the materials, prepared by the attrition mixing and coprecipitation. In the latter case chromia grains of smaller sizes occur, but no influence of this feature on the properties could be noticed (see Table 3).

The crack path behaviour observed in the TZP/Cr_2O_3 system is different from that in the TZP/carbide composite. The dominating crack path is through the chromia grains (Fig. 5).

Transmission electron micrographs indicate that the oxide inclusions adhere tightly unless the tetragonal to monoclinic transformation has taken place. Since this transformation was not observed in the polished samples it was believed that its appearance in some places of the thin sections had resulted from the impulse delivered by their preparation

Table 1. Specific surface area (S_w) of the starting powders

Powder	*Cr_3C_2*	*Cr_7C_3*	*Cr_2O_3*	*2·9Y-TZP*
S_w [m^2 g^{-1}]	16·0	15·6	21·8	7·5

Table 2. Properties of the composites in the TZP/chromium carbide system

Material	*Processing*	*Density, %theo.*	*Young modulus, MPa*	*Vickers hardness, GPa*	*Fracture toughness, MPa $m^{0.5}$*
TZP matrix	*HP, 1400°C*	*99·7*	*209 ± 3*	*14·1 ± 0·3*	*4·6 ± 0·1*
+ 10% Cr_3C_2	HP, 1400°C	97·3	213 ± 1	17·4 ± 0·6	5·4 ± 0.1
+ 20% Cr_3C_2	HP, 1400°C	97·1	213 ± 2	18·1 ± 0.6	5.2 ± 0.3
+ 10% Cr_7C_3	HP, 1400°C	99·3	218 ± 2	16·7 ± 0.6	6.2 ± 1.2
+ 20% Cr_7C_3	HP, 1400°C	99·0	224 ± 3	17·9 ± 0.7	8·7 ± 1·3
+ 10% Cr_3C_2	PS, 1500°C	93·2	176 ± 1	10·5 ± 1.0	—
+ 20% Cr_3C_2	PS, 1500°C	90·9	177 ± 2	11·8 ± 0·7	—
+ 10% Cr_7C_3	PS, 1500°C	92·9	171 ± 1	13·3 ± 0·9	—
+ 20% Cr_7C_3	PS, 1500°C	93·4	180 ± 1	13·5 ± 0·6	—

HP, hot-pressing; PS, pressureless sintering.

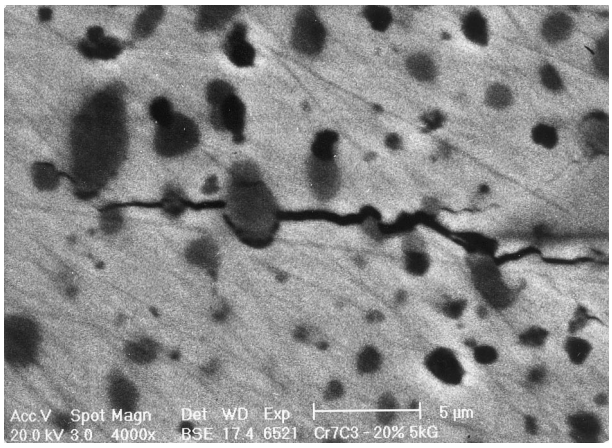

Fig. 2. SEM micrograph of the crack path in the hot-pressed TZP/Cr_7C_3 composite.

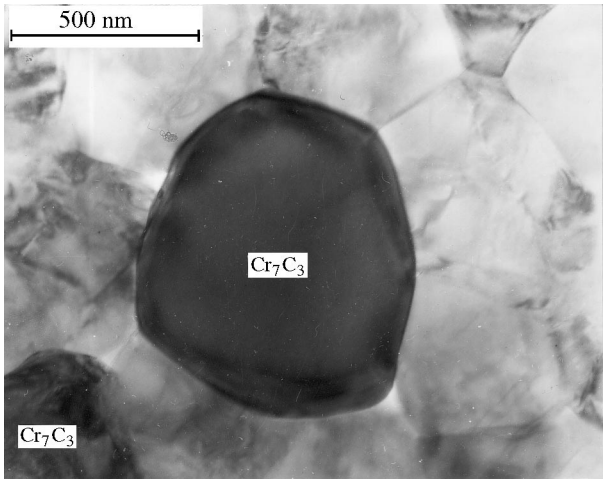

Fig. 3. TEM micrograph of the hot-pressed TZP/Cr_7C_3 composite.

procedure. At the TZP/Cr_2O_3 interfaces cracks are observed in the vicinity of the transformed zirconia grains (Fig. 6). No such cracks occur in the TZP/Cr_7C_3 system even in the neighbourhood of the transformed zirconia grains. Different behaviour of the both systems can plausibly be explained by the higher stresses in the TZP/oxide composite; they are generated from the $t \rightarrow m$ transformation and from the CTE mismatch. The latter factor seems to be of higher importance in the TZP/Cr_2O_3 system, as chromia coefficient of thermal expansion is smaller ($7{\cdot}5 \times 10^{-6}$ °C^{-6}) than that of the TZP ($11{\cdot}0 \times 10^{-6}$ °C^{-1}) and Cr_7C_3. The stresses generated in the inclusion particles are manifested by the strain contours present in the chromia (see Fig. 6(a)) and chromium carbide grains (not shown here) adjacent to the transformed zirconia particles.

In several places, within the TZP/Cr_2O_3 microstructure the incorporation of the chromia grains into the TZP monocrystalline grains occured (Fig. 6(b)). This phenomenon was not observed in the TZP/Cr_7C_3 system. The easy crack formation in the TZP/oxide composite can be postulated as the contributing factor to the fracture toughness increase.

4 Conclusions

Pressureless sintering at 1500°C of TZP/chromia carbide and TZP/chromia composites did not result in the dense materials. Much higher densification was achieved by the hot-pressing under 25 MPa at 1400°C. The composites show the increase of Young's modulus, hardness and fracture toughness compared to the TZP matrix.

The chemical reaction in the TZP/Cr_3C_2 system resulted in the Cr_7C_3 formation. Such composites were less densified, even under hot-pressing conditions and hence show worse properties.

Both studied systems differ in the crack propagation way. Transgranular cracks occur in the TZP/Cr_2O_3 system. On the contrary, crack deflection due to the secondary phase particles is observed in the TZP/Cr_7C_3 system. A close adherence of the inclusion and matrix particles is characteristic for the both studied systems.

Table 3. Properties of the composites in the TZP/Cr_2O_3 system

Material	*Processing*	*Density, %theo.*	*Young modulus, MPa*	*Vickers hardness, GPa*	*Fracture toughness, MPa $m^{0.5}$*
TZP matrix	*HP, 1400°C*	*99·7*	*209 ± 3*	*14·1 ± 0·3*	*4·6 ± 0·1*
+ 10% Cr_2O_3	M, HP, 1400°C	99·5	213 ± 1	18·1 ± 0·6	8·7 ± 1·2
+ 20% Cr_2O_3	M, HP, 1400°C	99·3	224 ± 2	19·6 ± 1·0	6·2 ± 1·0
+ 10% Cr_2O_3	C, HP, 1400°C	99·3	218 ± 2	18·6 ± 0·9	5·9 ± 0·4
+ 20% Cr_2O_3	C, HP, 1400°C	99·0	225 ± 5	20·0 ± 1·3	5·4 ± 0·3
+ 10% Cr_2O_3	M, PS, 1500°C	92·3	173 ± 2	12·8 ± 0·9	—
+ 20% Cr_2O_3	M, PS, 1500°C	91·0	163 ± 2	14·8 ± 1·4	—
+ 10% Cr_2O_3	C, PS, 1500°C	94·9	172 ± 6	14·3 ± 0·7	—
+ 20% Cr_2O_3	C, PS, 1500°C	95·3	198 ± 9	15·0 ± 0·2	—

M, mixing; C, coprecipitation.

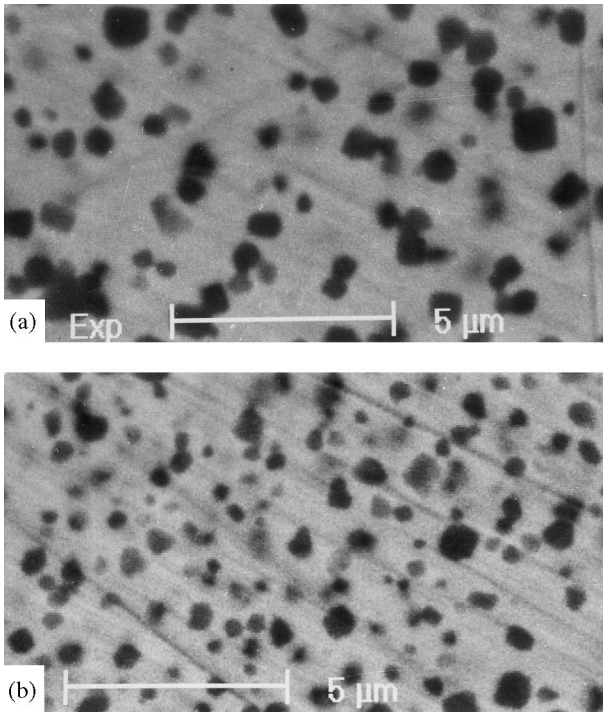

Fig. 4. SEM micrographs of the polished surface hot-pressed composites in the TZP/Cr_2O_3 system. A—20 vol% of chromia added by the mixing; B—20 vol% of chromia coprecipitated with zirconia.

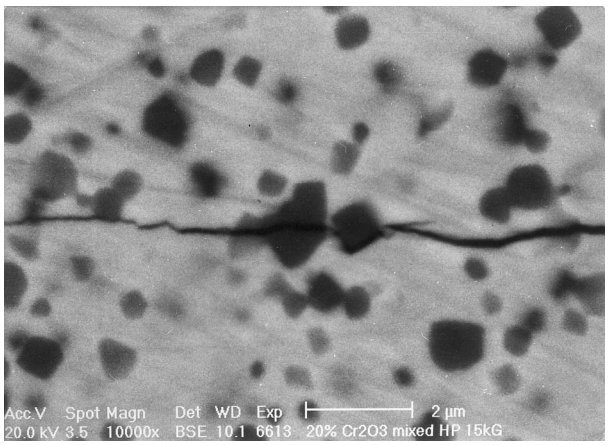

Fig. 5. SEM micrograph of the crack path in the hot-pressed TZP/Cr_2O_3 composite.

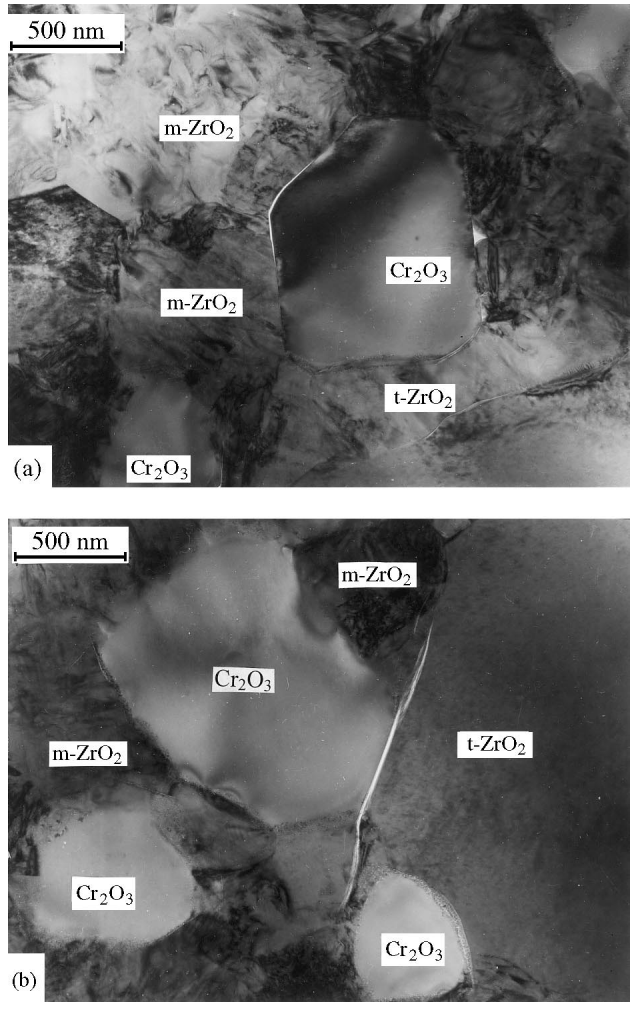

Fig. 6. TEM micrographs of the hot-pressed TZP/Cr_2O_3 composite.

The $t \rightarrow m$ phase transformation in the matrix as well as the CTE mismatch result in the tangential cracks at the TZP/Cr_2O_3 interface. No such cracks occur in the TZP/Cr_7C_3 system.

The SEM and TEM observations allow to suggest the dominating toughening mechanisms in the studied systems. Most probably this can be attributed to the crack deflection phenomenon in the TZP/Cr_7C_3 system and the microcracks present in

the TZP/Cr_2O_3 composite. Of course transformation toughening, characteristic for the tetragonal zirconia polycrystals is operating in each case.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research under grants no. 7 T08D 019 10 and 7 T08A 052 10.

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