A TZP matrix composite with in situ grown TiC inclusions

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Abstract

A TiO_2–Y_2O_3–ZrO_2 solid solution was prepared by the coprecipitation–calcination technique. The resulting powder of $+100$ m^2/g specific surface area was mixed with a phenol-formaldehyde resin whose in situ thermal decomposition resulted in carbon formation. The reaction of the carbon and Ti coming from the solid solution gave TiC evenly distributed within the system. Hot-pressed samples showed hardness higher than conventional TZP bodies. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Hardness; Particulate composites; TiC; Zirconia solid solutions; ZrO_2

1. Introduction

The high fracture toughness and strength of tetragonal zirconia polycrystals (TZP) are due to the tetragonal to monoclinic zirconia solid solution transformation (t→m) at the crack tip advancing through the material. This transformation consumes strain energy otherwise available for crack propagation. The relatively low hardness of these materials limits their potential applications. Numerous investigations proved that hard carbide inclusions incorporated into the TZP matrix resulted in materials of higher hardness and fracture toughness. This was demonstrated to be the case for SiC whiskers[1,2] for platelets[3] and for isometric particles.[4]

In the last years several composite systems containing carbide inclusions in the zirconia matrix were investigated in our laboratory.[5–10] The inclusions encompassed WC, W_2C, SiC, Cr_3C_2, Cr_7C_3, TiC. These materials showed better mechanical properties than the "pure" matrix (Y-TZP) material. Physical mixing of the composite constituent powders was applied in the previous study. The aim of the present work was to check the possibility of synthesis of evenly distributed TiC inclusions in the TZP matrix by a chemical route.

Thermodynamic calculations in the TiO_2–C and ZrO_2–C systems show that the related carbides can be synthesised if the CO partial pressure in the surrounding atmosphere is lower than that indicated in Fig. 1.[11]

Titanium carbide exists under much higher CO pressures than zirconium carbide. So, one can expect that in the case of a physical mixture of the two oxides and carbon the first product of the reaction should be TiC.

The present work is based on the experimentally confirmed assumption that Ti can be extracted with carbon from the solid solution in the TiO_2–Y_2O_3–ZrO_2 system.[12] It should result in titanium carbide formation.

2. Experimental

2.1. Powder synthesis

Based on our earlier studies[13–17] a solid solution powder of composition 18 mol% TiO_2, 3 mol% Y_2O_3 and 79 mol% ZrO_2 was prepared by the coprecipitation technique. The mixed aqueous solution of $ZrOCl_2$, YCl_3 and $TiCl_4$ (2.1 mol/dm^3) was introduced to a vigorously stirred aqueous solution of ammonia (2.5 mol/dm^3). Relatively high concentrations of the starting metal salt solution resulted in a fluffy gel. Its calcination led to a crystalline powder composed of porous, mechanically weak agglomerates.[18] Fig. 2 demonstrates the DTA and TG curves of the coprecipitated gel. The characteristic exothermic peak (maximum at 625°C) corresponds to the crystallisation of the solid solution. An X-ray diffraction pattern of the powder crystallised by the gel calcination for 1 h at 650°C is shown in Fig. 3. All reflections are ascribed to zirconia solid solutions of tetragonal and monoclinic symmetry. Using the Porter

and Heuer formula,[19] the proportions of the phases were determined. Based on the Scherrer equation the crystallite sizes of both phases were measured. A rather low calcination temperature led to a powder of high specific surface area. It was also measured by nitrogen adsorption using the BET isotherm. Characteristics of the powder are shown in Table 1.
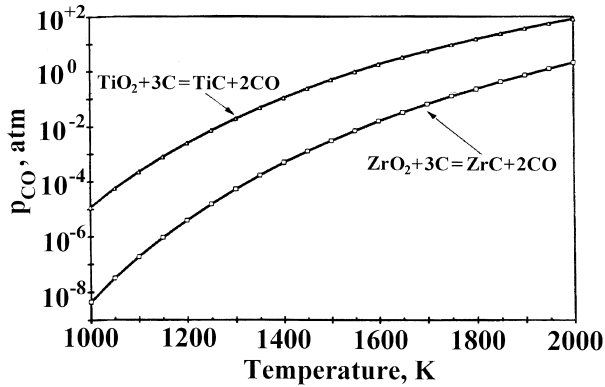

Fig. 1. Limit CO partial pressure for the indicated reactions. The reactions are arrested under pressures higher than indicated by the plots.
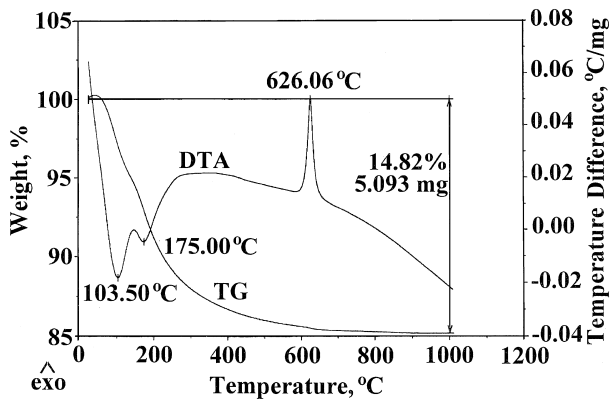

Fig. 2. DTA and TG curves of the coprecipitated gel. Rate of temperature increase 10°C/min.
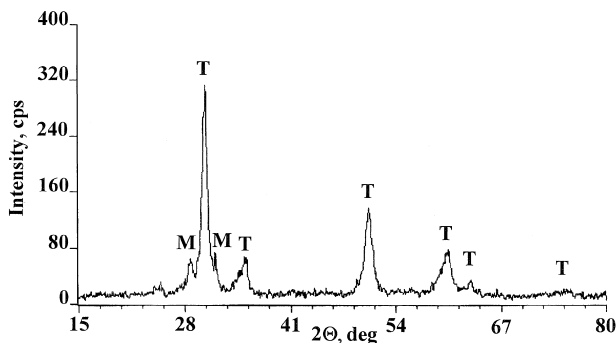
2.2. Preparation of composite powders

Using a similar concept as that developed by Greil[20] carbon was introduced into the system by mixing the powder with an ethanol solution of phenol-formaldehyde resin. Drying the solvent allowed us to distribute evenly the resin within the powder. The decomposition of the resin at 850°C in an argon atmosphere led to the intimate mixing of carbon and the zirconia solid solution powder. The samples, containing from 60 to 160% of carbon additive with relation to the stoichiometry of the TiO_2 and C reaction, were heat treated in an argon atmosphere in graphite crucibles for 2 h at 1300 and 1500°C with 10°C/min rate of temperature increase. X-ray diffraction measurements (Figs. 4 and 5) revealed TiC within the whole range of compositions and temperatures of heat treatment. Additionally in the samples of carbon content of 120% and higher fired at 1500°C, ZrC was observed (Fig. 5). The dominating zirconia phase was the one of tetragonal symmetry. Small amounts of monoclinic zirconia also occur.

The DTA and TG measurements were performed in air. The powders synthesised by the described method, showed a mass increase accompanied by the exothermic effect (Fig. 6). The peak temperature was of 503°C. At still higher temperature some mass decrease occurred.

The X-ray diffraction patterns of samples heated in air to the peak temperature and quickly cooled down showed reflections of TiO_2 (anatase). This fact suggests

Table 1
Characteristics of the 18 mol% TiO_2–3 mol% Y_2O_3–79 mol% ZrO_2 powder

Specific surface area (m²/g)	Monoclinic phase (vol.%)	Tetragonal phase (vol.%)	Monoclinic phase crystallite size (nm)	Tetragonal phase crystallite size (nm)
104	18.9	81.1	11.2 (111) 11.0 (111)	10.9 (111)

Fig. 3. X-ray diffraction pattern of the TiO_2–Y_2O_3–ZrO_2 solid solution powder. T and M stand for the tetragonal and monoclinic phases, respectively. CuK_α radiation.
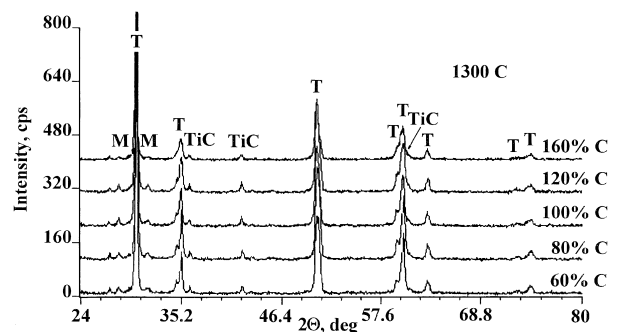

Fig. 4. X-ray diffraction pattern of powders, heat-treated at 1300°C. CuK_α radiation.

that the exothermic effect should be attributed to the TiC oxidation. Thus, the small weight loss at higher temperatures corresponds, most probably, to the oxidation of the non-reacted carbon. On this basis the carbon content could be determined. Weight increase due to the carbide phase oxidation was higher, the higher the carbon concentration. This suggests an increase of the carbon phase content with increased carbon additive. Table 2 demonstrates the results.

Only three TiC reflections of indices (111), (200), (220) were sufficiently strong to assess TiC lattice parameters. Their changes with carbon additive for the samples heat-treated at 1500°C are shown in Fig. 7. The data indicate that a carbon deficit compound comparing to the TiC formula was formed under the applied manufacturing conditions. Using the composition dependence of the TiC lattice parameter[21] the formulae shown in Fig. 7 could be suggested. The deoxidation of zirconia, most probably, consumed part of the carbon introduced to the system. These phenomena as well as the creation of ZrC in the samples of higher carbon content were the competitive processes to the formation of

titanium carbide. It seems to be the possible reason for the formation of titanium carbide with a carbon deficit.

2.3. Composite microstructure, properties and manufacturing

The powder with the carbon additive of 100%, was selected for sintering experiments. It was calcined at 1500°C for 1 h. The specific surface area of the powder was 3.2 m²/g. Attrition milling increased this value up to 10.6 m²/g. The powder was hot-pressed at 1400, 1450 and 1500°C under 25 MPa pressure with 1 h soaking at each temperature. The rate of temperature increase was 10°C/min.

The X-ray diffraction of the sintered samples (Fig. 8) revealed only titanium carbide and zirconia phases. The latter was mainly of tetragonal symmetry. Traces of monoclinic zirconia occurred in the material densified at 1400°C.

Fig. 9 shows the SEM micrograph of the material hot-pressed at 1500°C. The EDS analysis of the dark, evenly distributed spots indicates the titanium reach phase (Fig. 10a). These spots correspond plausibly to the non-stoichiometric titanium carbide inclusions. Their sizes
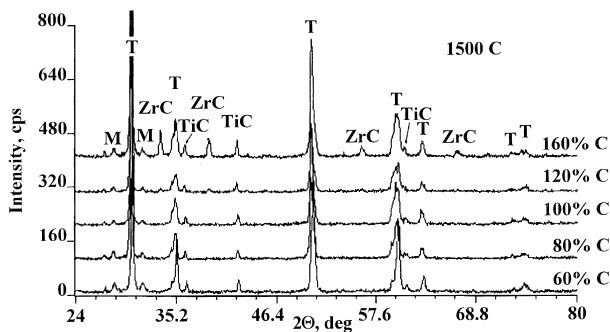

Fig. 5. X-ray diffraction pattern of powders, heat-treated at 1500°C. CuK$_\alpha$ radiation.
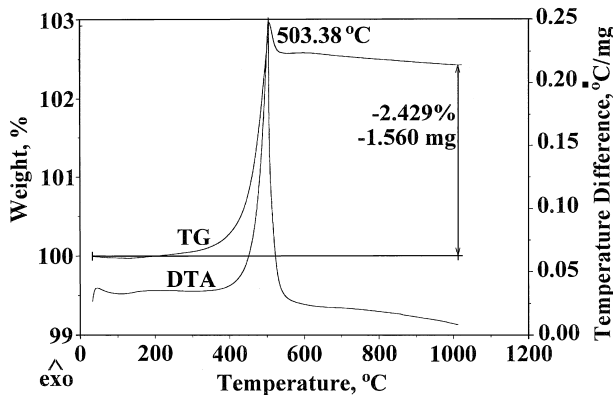

Fig. 6. DTA and TG curves of the powder heat treated at 1500°C. The carbon additive in the original solid solution powder corresponded to 80% of the amount coming from the stoichiometry of the TiO$_2$ and C reaction. Heating rate 10°C/min. Sample mass 64.2218 mg. Air atmosphere.

Table 2
Carbon content and weight increase due to carbide phase oxidation in the powders heat treated at indicated temperatures

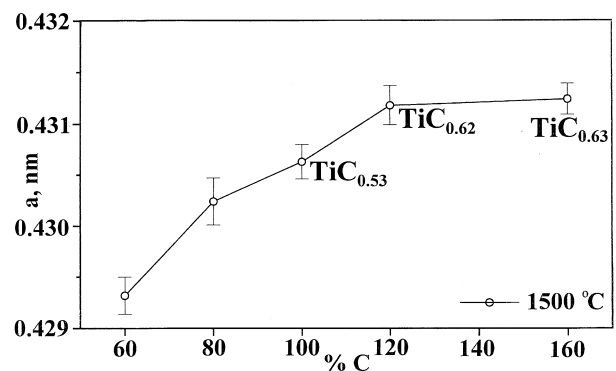| Synthesis temperature, °C/C added (%)	Weight increase due to carbide phase oxidation (%)	C (wt.%)
1500/60	2.3	0.16
1500/80	3.0	0.53
1500/100	3.7	0.79
1500/120	4.1	0.90
1500/160	6.3	1.95
1300/60	2.1	2.18
1300/80	2.2	2.31
1300/100	2.3	2.33
1300/120	2.4	2.53
1300/160	2.4	4.10

Fig. 7. Titanium carbide lattice parameter vs. carbon content in the system calcined at 1500°C.

do not surpass 0.5 µm. The zirconium signal results probably from the limited resolution of the applied method.

In the bright areas zirconium is the prevailing component (Fig. 10b). However, a signal coming from titanium is also present. Since, zirconia grains are several times larger than the carbide ones, this effect cannot be attributed to the limited resolution of the applied analytical method. So, not all titanium was extracted from the zirconia solid solution during the reaction. This conclusion seems to be corroborated by the computer analysis of several pictures like Fig. 9. The analysis indicated the volume fraction of titanium carbide equal to 8.27 ± 1.05 vol.%. This corresponds to the weight fraction of TiC of 6.45 wt.%. (Calculations were made assuming the density of TiC to be 4.93 g/cm^3 and that of ZrO_2 s.s. to be 6.03 g/cm^3.) The total amount of titanium available in the system allows the formation of TiC of 9.39 wt.%, i.e. higher than the fraction found experimentally.

Some further information on the microstructure of the studied material was provided by the transmission electron micrograph observations. One of them is shown in Fig. 11. In numerous areas fine inclusions could be noticed in the larger grains. The EDS chemical analyses revealed that these inclusions were composed of Ti, Zr, O and C (Fig. 12a and b). However, the surroundings of these inclusions are composed of titanium carbide only (Fig. 12c). It cannot be ignored that the
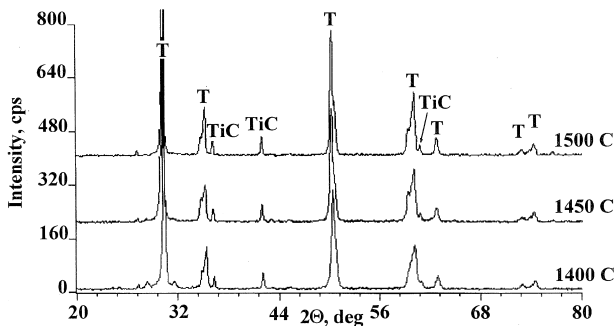

Fig. 8. X-ray diffraction patterns of the samples hot-pressed at indicated temperatures.
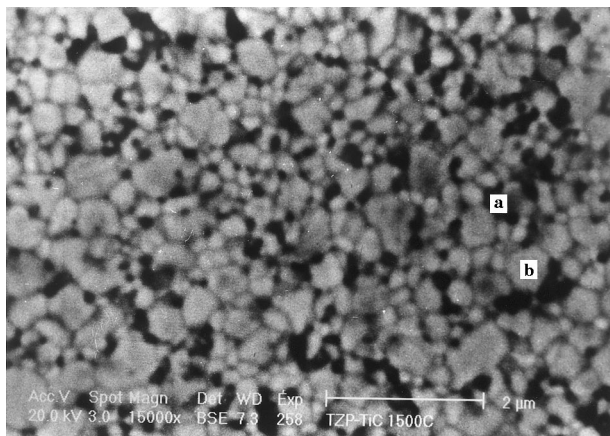

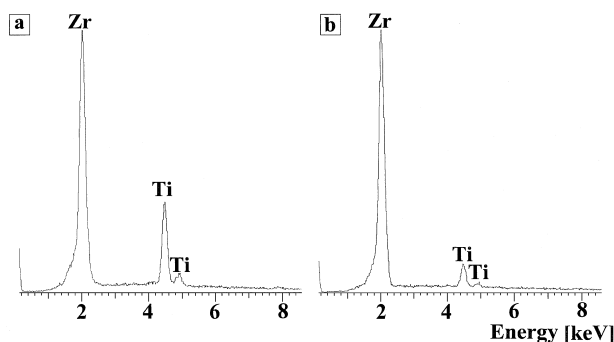Fig. 9. SEM micrograph of the composite hot-pressed at 1500°C.

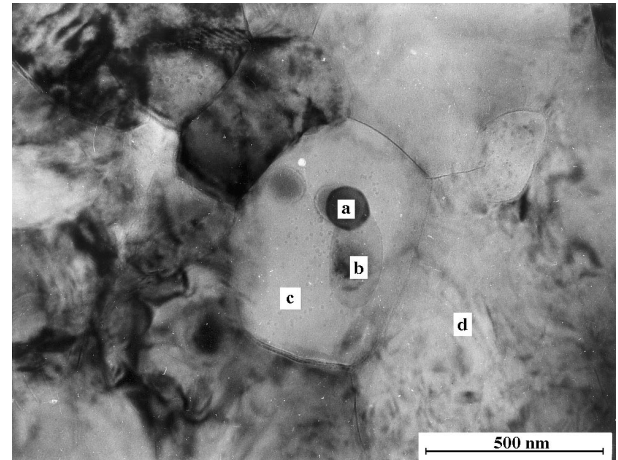Fig. 10. EDS analyses of the areas indicated in Fig. 9.

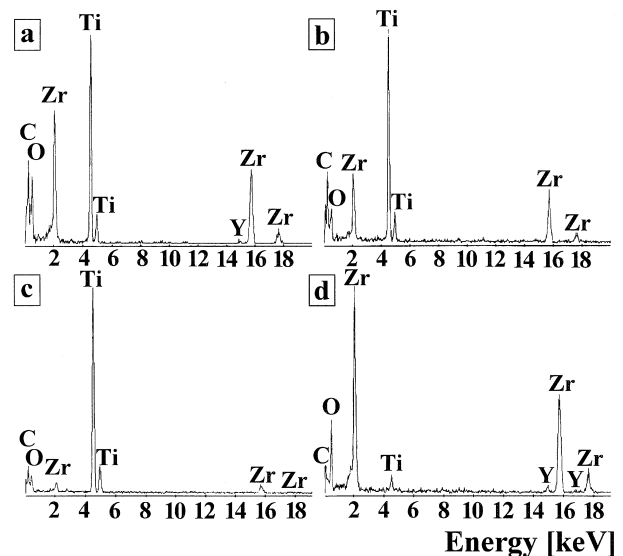Fig. 11. TEM micrograph of the same sample as in Fig. 9.

Fig. 12. EDS analysis of the areas indicated in Fig. 11.

Table 3
Properties of the composites

Hot-pressing temperature (°C)	Apparent density (g/cm^3)	Relative density[a] (%theo.)	HV (GPa)	K_{Ic} (MPa m$^{1/2}$)	(E GPa)
1400	5.61±0.03[b]	94,4	14.7±1.9	3.9±0.2	191.9±8.8
1450	5.81±0.01	97.8	14.9±1.3	4.2±0.2	215.0±3.3
1500	5.84±0.01	98.3	17.0±1.4	4.1±0.2	221.3±1.7

[a] Based on the physical density of 5.94 g/cm^3.
[b] Denotes confidence interval at confidence level of 0.95.

small inclusions are the zirconia s.s. Therefore, the presence of Ti and C in the signal results from the underlying titanium carbide. This can be imagined as a "sandwich" structure. Fig. 12d demonstrates that zirconia grains also, occur with some titanium present in the solid solution.

Composite hardness (HV) and fracture toughness (K_{Ic}) were measured by the Vickers indentation method. The ultrasonic method was applied to determine Young's modulus (E). Apparent density was determined by the hydrostatic weighing. All these data are shown in Table 3. The rather low fracture toughness of the material can be attributed to the relative increase of Y_2O_3 concentration in zirconia. This increase results from the extraction of TiO_2 from the solid solution. As is well known, Y_2O_3 stabilises the high symmetry ZrO_2 modifications. A similar effect arises from the deoxidation of zirconia systems.[22] The reduction process undoubtedly occurs under the oxygen free manufacturing conditions. Both factors i.e. the increased Y_2O_3 concentration in the ZrO_2 solid solution and the reduction of the system make tetragonal zirconia less susceptible to its transformation to the monoclinic form. So, the transformation toughening mechanism becomes less effective.

3. Conclusions

(i) Titanium is extracted with carbon from the solid solution in zirconia. The reaction results in a carbon deficient titanium carbide.

(ii) The microstructure of the dense body contains small (<0.5 μm) titanium carbide inclusions evenly distributed among the zirconia grains. But in several cases zirconia inclusions in the titanium carbide grains were observed.

(iii) Hot-pressing at 1500°C under 25 MPa results in a material of density +98% of the theoretical.

(iv) The material shows hardness and Young's modulus higher than usually observed in TZP bodies.

(v) The rather low toughness of the material can be attributed to the relative increase of Y_2O_3 concentration in the solid solution due to the decreased concentration of TiO_2 extracted with carbon. Another phenomenon important from this point of view is the reduction process

in the zirconia material. Both factors make the transformation toughening less effective.

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