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Thermal stability of tungsten carbide in 7 mol.% calcia–zirconia solid solution matrix heat treated in argon

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Abstract

Zirconia polycrystals stabilised with 7 mol.% CaO containing 10 vol.% WC particles (Ca-PSZ/WC) were obtained by using zirconia nanopowder and WC micropowder. Cold isostatically pressed samples were pressureless sintered in argon at 1350–1950 °C. The influence of the sintering temperature and the incorporation of WC particles on the phase composition and mechanical properties of the composites were studied. Decomposition of WC due to the reaction with the zirconia matrix was found. W_2C and metallic tungsten were detected as decomposition products when heat treated below 1750 °C. At higher temperatures, ZrC is formed. The mechanism of WC decomposition was discussed. The zirconia polycrystals modified with in situ formed W and W_2C inclusions showed a bending strength of 417 ± 67 MPa, a fracture toughness of 5.2 ± 0.3 MPa $m^{0.5}$ and a hardness of 14.6 ± 0.3 GPa.

Keywords: ZrO_2; Composites; Inclusions; WC; Mechanical properties

1. Introduction

Stability of tungsten carbide in contact with zirconia solid solutions at elevated temperatures is an important issue for the production and utilization of zirconia based composites reinforced with WC inclusions. Until now, reactivity of yttria–zirconia solid solution with reference to WC particulates has only been studied. Haberko et al.[1] reported the presence of W_2C and ZrC in the Y-TZP/WC composites heat treated at 1500 °C in a carbon bed. It was stated that both W_2C and ZrC originated from the reaction between ZrO_2 and WC. The formation of ZrC in the reaction of ZrO_2 and C (carbon bed) was also considered but its contribution to the overall ZrC detected was not determined.

Development of composites in the $CaO–ZrO_2–WC$ system[2,3] created the necessity to study the thermal stability of WC particulates also in contact with calcia–zirconia solid solutions. The presented work is devoted to this issue. The main aim was to quantitatively characterise the evolution of phase composition of the Ca-PSZ/WC composites heat treated in a broad temperature range to establish the mechanism of tungsten carbide decomposition in contact with zirconia solid solutions. The effect of the WC decomposition on the mechanical properties of the Ca-PSZ/WC composites was also studied.

2. Experimental procedure

Zirconia polycrystals which contained 7 mol.% CaO in solid solution and 10 vol.% WC particulates as an original additive (Ca-PSZ/WC) were prepared using zirconia nanopowder and tungsten carbide micropowder. A co-precipitation method followed by hydrothermal crystallization was used to prepare the zirconia nanopowder. A homogeneous calcia–zirconia hydrogel was co-precipitated from an aqueous solution of appropriate chlorides with NaOH at a pH of 12.5. The following chemical reagents were used: $ZrOCl_2 \cdot 8H_2O$—zirconia content >99.7% (main impurity measured by AAS was Si—0.03%, Fe—0.02%, Al—0.015%), Beijing Chemicals Import and Export Corporation, China; $CaCO_3$—analytically pure, Polish Chemical Works, Gliwice, Poland; NaOH—analytically pure, Polish Chemical Works, Gliwice, Poland. The hydrogel was hydrothermally treated for 4 h at 240 °C under the pressure of saturated water

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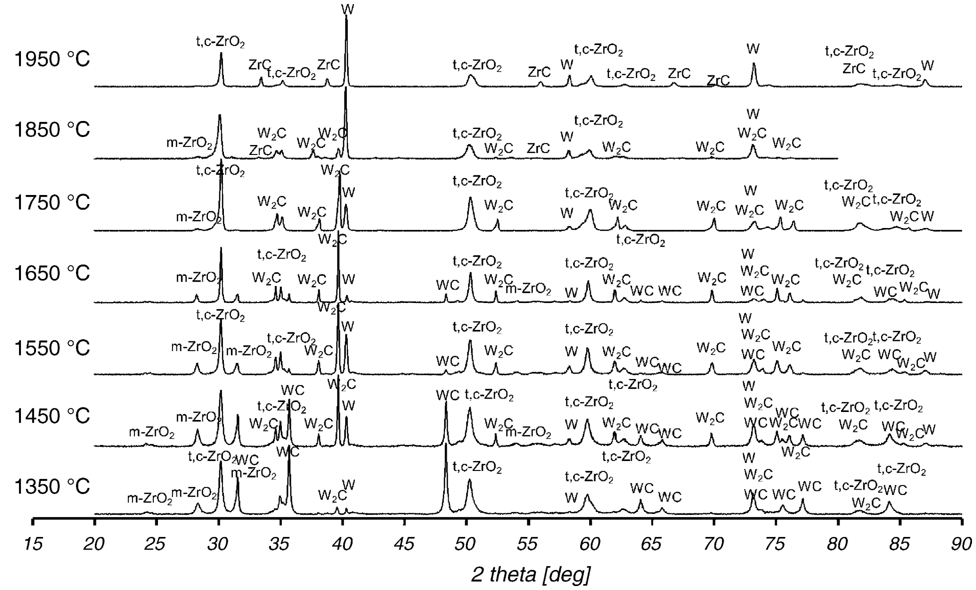

Fig. 1. X-ray diffraction patterns of the Ca-PSZ/WC composites as a function of the sintering temperature.

vapour (~3.8 MPa). The crystalline zirconia powder with a specific surface area of 54.3 ± 1.0 m^2/g was composed of a mixture of equiaxed crystallites of 10 nm and needle like shape of 30–64 nm in width and of a ratio of length to width ranging from 2.5 to 5.6. The isometric and elongated crystallites had tetragonal and monoclinic symmetry, respectively. The monoclinic phase content was 50 ± 2 vol.%. Details concerning powder characterization methods can be found in Ref. [4].

The original WC powder (Baildon, Katowice, Poland) was milled for 40 h in a rotary–vibratory mill with zirconia grinding media of 10 mm in diameter in distilled water to reduce the modal value of the particle size from 10 to 0.59 μm as measured by the sedimentation method (Sedigraph 5100, Micromeritics).

The WC and zirconia powders were homogenised by wet attrition for 1 h with zirconia grinding media of 2 mm in diameter in isopropyl alcohol then dried and cold isostatically pressed at 200 MPa into disks of 12 mm in diameter and 4 mm thick. After placing between the two graphite foil dividers, the samples were pressurelessly sintered for 1 h at 1350–1950 °C in a flow (0.11 m^3/h) of argon (99.99%). One series of the sintering experiments was performed. A furnace with a graphite heater, a heating rate of 15 °C/min and a cooling rate of 35 °C/min was used. Ca-PSZ samples material without WC were also prepared under the same conditions. For the purpose of bending tests, the plates of 25 mm × 30 mm were prepared.

The phase composition of the sintered materials was determined by X-ray diffraction analysis (radiation—Cu $K\alpha_1$, range—20–90° 2θ, step—0.008° 2θ). Before measurement, a surface layer of each sample, which included ~30% of the original thickness, was removed by grinding and the surface was finally polished with 1 μm diamond powder. Rietveld refinements were carried out by means of the X'Pert Plus v1.0 program (Philips) to determine phase fractions and unit cell parameters of the constituent phases. Because of the complex phase composition of some samples, densification of the sintered polycrystals was determined using optical microscopy and direct porosity measurements. Surface areas of 500 μm × 500 μm were numerically analysed (Image J 1.29x—Ref. [5]). The relative density was calculated by subtracting the mean percentage pore content (taken from three measurements) from 100%. Polished and thermally etched surfaces (vacuum, 1250 °C for 6 h) were observed under SEM to monitor changes in the microstructure due to the WC incorporation and the sintering temperature.

Vickers hardness was measured under a load of 9.81 N. Fracture toughness, K_{Ic}, was determined by Vickers indentation. A load ranging from 29.4 to 98.1 N and a holding time of 10 s were used. The Palmqvist crack model was applied for the K_{Ic} calculations.[6] Bending strength of the samples of 1.5 mm × 2.5 mm × 25 mm was measured by the three-point method, using a span of 20 mm and a loading rate of 2 mm/min. The samples for mechanical property measurements were polished with 1 μm diamond paste.

3. Results

The evolution of the phase composition of the Ca-PSZ/WC composites with sintering temperature is shown in Figs. 1–3. The X-ray diffraction analysis revealed the presence of cubic, tetragonal and monoclinic zirconia polymorphs, WC, W_2C, metallic tungsten and ZrC in the studied materials. The phase content depends on the sintering temperature. W_2C and W as WC decomposition products were observed in the samples sintered at temperatures as low as 1350 °C. WC disappeared at 1750 °C, and the remaining W_2C decomposed completely to tungsten at 1950 °C. Zirconium carbide has been found in the samples sintered above 1750 °C.

The influence of the sintering temperature and the WC incorporation on the cubic, tetragonal and monoclinic phase content is shown quantitatively in Fig. 2. An increase of the cubic phase content and a decrease of the sum of the tetragonal and

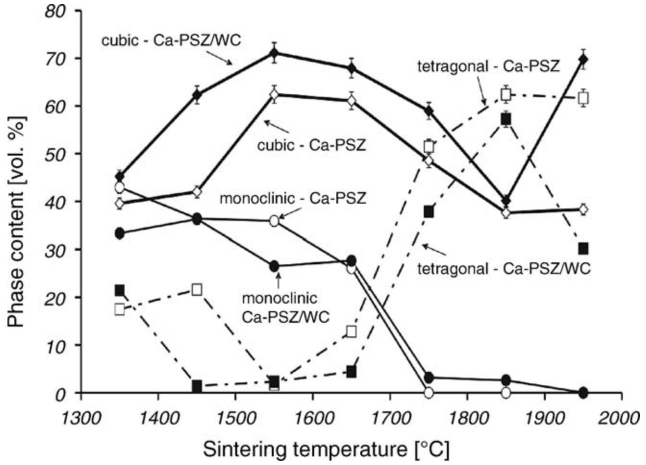

Fig. 2. The zirconia phase content in the Ca-PSZ material and the zirconia matrix of the Ca-PSZ/WC composite as a function of the sintering temperature.

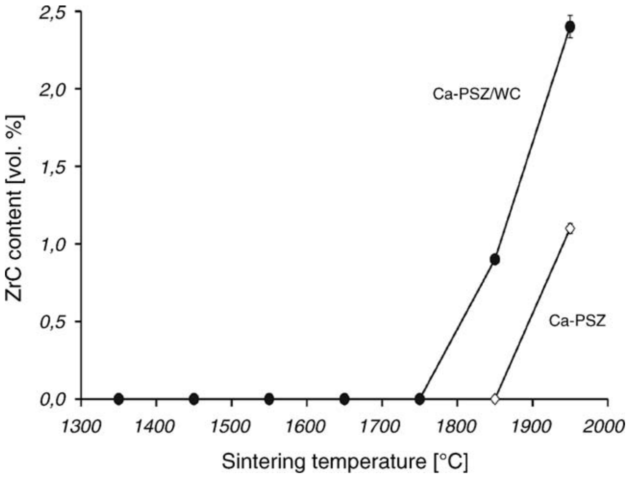

Fig. 4. The zirconium carbide content in the Ca-PSZ and Ca-PSZ/WC materials as a function of the sintering temperature.

monoclinic phase is observed at temperatures below 1550 °C. This behaviour is similar to that predicted by the CaO–ZrO_2 phase diagram for the phase equilibrium in air[7] and originated mainly from changes in the CaO distribution between tetragonal and cubic polymorph. At higher sintering temperatures, both the cubic and monoclinic phase content decrease whereas the tetragonal phase content increases. This behaviour is most probably related to the oxygen nonstoichiometry of ZrO_2 due to sintering at low oxygen partial pressure.[8–10] A redistribution of the Ca stabiliser should also be considered as a factor influencing stability of both phases. The incorporation of WC particulates into the Ca-PSZ matrix increased the cubic phase content and slightly decreased the tetragonal phase content. The content of the monoclinic phase remained practically unchanged.

Changes in the WC, W_2C and W content in the Ca-PSZ/WC composites with sintering temperature shown in Fig. 3, indicate a small and non-monotonic increase of the tungsten content and a significantly larger increase of the W_2C content in the temperature range in which WC exists. In this temperature range ZrC is not observed (Fig. 4). This proves that WC decomposes to W_2C and W and this process is not accompanied by the formation of ZrC. The non-monotonic course of the W and WC content at 1550–1750 °C indicates a sensitivity of the WC decomposition to fluctuation of the sintering atmosphere composition, which is probable at the applied experimental procedure. The presence of a small content of ZrC in the Ca-PSZ and Ca-PSZ/WC materials (Fig. 4) confirms the reaction between ZrO_2 and C above 1750 °C. Potential carbon sources are as follows: (i) the graphite foil, (ii) the furnace atmosphere, (iii) the W_2C decomposition. The graphite foil together with the carbon rich atmosphere contacting with the zirconia-based sample develops the carburisation effect. Thickness of the carburizing surface layer of 690 and 800 μm can be estimated by approximation of the data reported by Zhao et al.[11] for the sintering temperatures of 1850 and 1950 °C, respectively. These values are comparable or larger then the thickness of the surface layer removed from the studied Ca-PSZ and Ca-PSZ/WC samples before the X-ray measurements indicating that the effect of the first two carbon sources can be neglected at least below 1750 °C. Above this temperature, the additional amount of ZrC might be formed in the Ca-PSZ/WC sample from carbon originated from the W_2C decomposition as indicated by the higher ZrC content of the Ca-PSZ/WC composites than that of the original Ca-PSZ material (Fig. 4). The measured difference of the ZrC content between the Ca-PSZ/WC and Ca-PSZ sample is 0.9 and 1.2 vol.% at 1850 and 1950 °C, respectively. Simple calculations indicate that a comparable ZrC amount of 1.6 vol.% can be formed during the reaction between ZrO_2 and the carbon released from 6.2 vol.% W_2C measured in the Ca-PSZ/WC sample at 1750 °C. This suggests that the WC decomposition is accompanied by the ZrC formation when the conditions for carbothermal reduction of ZrO_2 are induced.

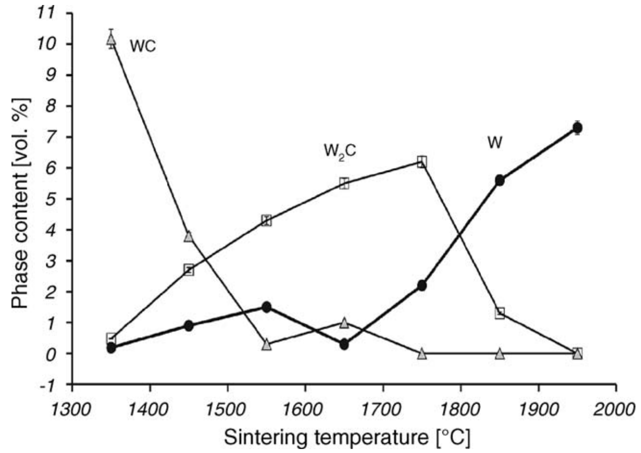

Fig. 3. The WC, W_2C and W content in the Ca-PSZ/WC composites as a function of the sintering temperature.

The WC decomposition results in an increased porosity of the Ca-PSZ/WC composites (Fig. 5). This suggests the formation of gaseous products which inhibit densification of the composites. The decreased density of the Ca-PSZ materials with sintering temperature is related most probably to the high heating rate which enhances the disadvantageous effects of differential sintering of the nanopowders.[12]

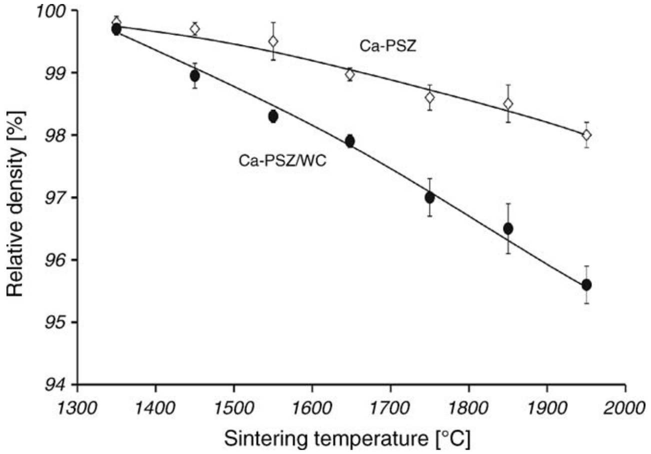

Fig. 5. Relative density of the Ca-PSZ and Ca-PSZ/WC materials as a function of the sintering temperature.

WC, W_2C and W inclusions were uniformly distributed within the composite microstructure (Fig. 6a and b). There were no significant changes in morphology of the inclusions before and after WC decomposition. Some intergranular WC inclusions which dominated in the composites sintered at low temperatures changed to intragranular ones as a result of zirconia grain growth in the high temperature sintered composites. The ZrO_2 grain size was significantly inhibited by the WC, W_2C and W inclusions when compared to the zirconia grain growth observed in the Ca-PSZ materials (Fig. 6).

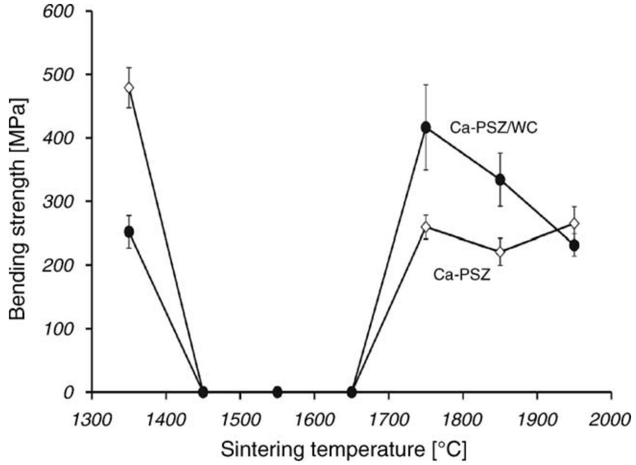

Fig. 7. Bending strength of the Ca-PSZ and Ca-PSZ/WC as a function of the sintering temperature.

The mechanical properties of the studied materials are presented in Figs. 7 and 8. The fracture strength (Fig. 7) dropped almost to zero for the materials sintered at 1450–1650 °C due to the extended t → m transformation during cooling and the presence of cracks. However, the progress in deoxidation of the zirconia solid solution which resulted in the reduced amount of the monoclinic phase raised the bending strength over 250 MPa at higher sintering temperatures. The microstructural and phase changes that accompanied the incorporation and decomposition of WC further increased the bending strength. A value

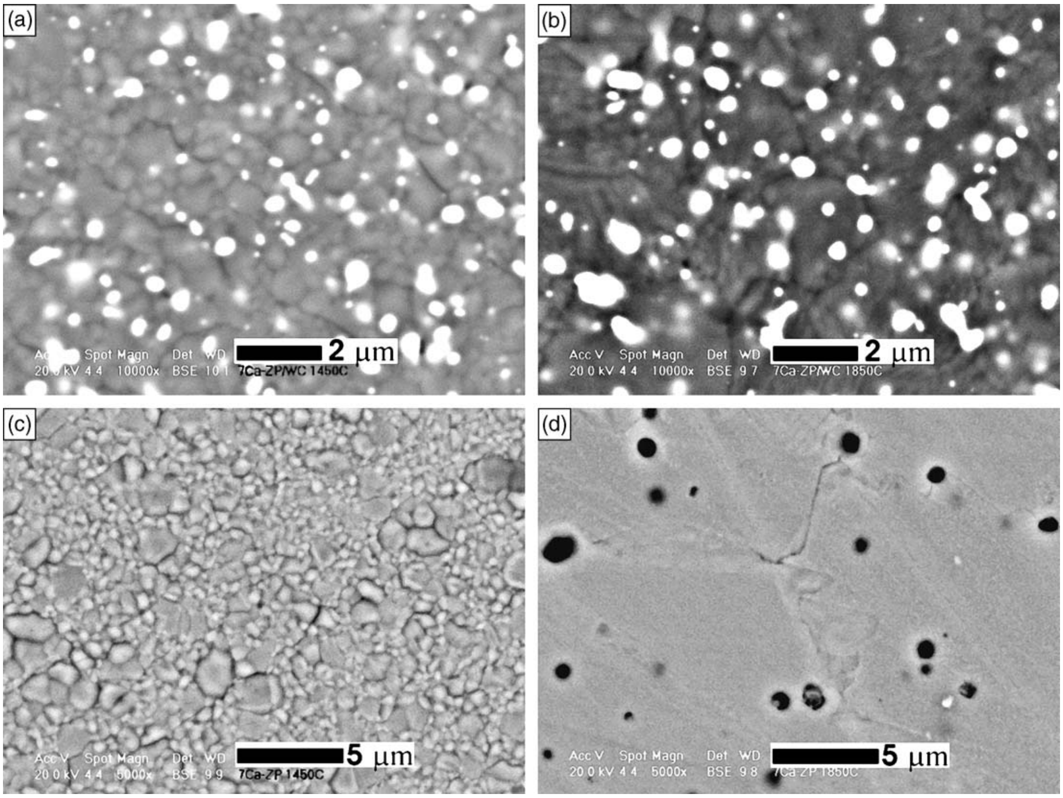

Fig. 6. Back scattered SEM micrographs: (a) Ca-PSZ/WC sintered at 1450 °C, (b) Ca-PSZ/WC sintered at 1850 °C, (c) Ca-PSZ sintered at 1450 °C, (d) Ca-PSZ sintered at 1850 °C.

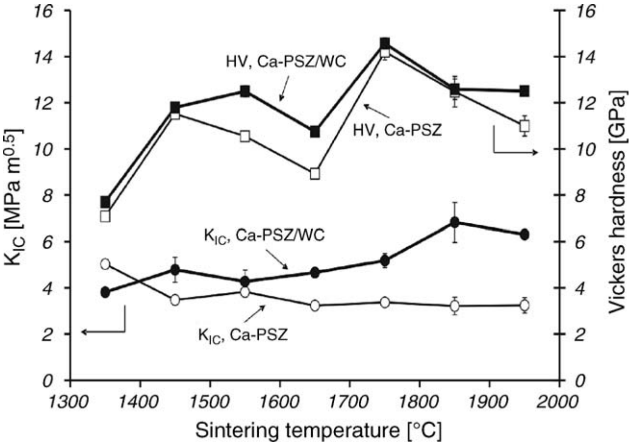

Fig. 8. Fracture toughness and Vickers hardness of the Ca-PSZ and Ca-PSZ/WC as a function of the sintering temperature.

of 417 ± 67 MPa was measured for the Ca-PSZ/WC composite sintered at 1750 °C. This material showed also the highest hardness of 14.6 ± 0.3 GPa and increased fracture toughness of 5.2 ± 0.3 MPa $m^{0.5}$ (Fig. 8). The increase of porosity degraded bending strength of the composites sintered above 1750 °C. In contrast, a significant rise (95–112%) in fracture toughness of the composites compared to the Ca-PSZ material has been found for the sintering temperature range of 1850–1950 °C in which in situ formed tungsten inclusions prevailed.

An increase in the hardness by18.4 and 20.4% was measured in the Ca-PSZ/WC composites sintered at the temperature of 1550 and 1650 °C, respectively (Fig. 8). This coincides with the increase in the W_2C content by up to 70% of the WC + W + W_2C sum. A W_2C hardness of 58 and 40 GPa was calculated using the rule of mixture and assuming a hardness of 22 and 3.2 GPa for WC[13] and W,[14] respectively. These values are larger than a W_2C hardness of 22 GPa reported in literature[15] suggesting that the possible mechanism of the hardness increase is related not to the hardness of W_2C being similar to WC but to stresses generated in the zirconia matrix due to the W_2C appearance. W_2C has ~9% larger physical density, 30–40% smaller modulus of elasticity and larger thermal expansion anisotropy (W_2C: $\alpha_a = 1.2 \times 10^{-6}\,K^{-1}$, $\alpha_c = 11.4 \times 10^{-6}\,K^{-1}$; WC: $\alpha_a = 5.2 \times 10^{-6}\,K^{-1}$, $\alpha_c = 7.3 \times 10^{-6}\,K^{-1}$)[16] than WC. Synergetic effects of these factors are most probably responsible for the observed hardness increase of the Ca-PSZ/WC composites. Above 1650 °C, the increase of both porosity and the low hardness secondary phase of metallic tungsten significantly reduced the hardness increase of the Ca-PSZ/WC composites.

4. Discussion

The X-ray diffraction analysis of the phase composition evolution during sintering Ca-TZP/WC composites together with porosity measurements provided evidence that WC inclusions inserted into a matrix of zirconia solid solution decomposed in two stages. The first one is connected with the W_2C formation. In the second one, W_2C decomposed giving metallic tungsten. In both stages carbon has evolved which reacted with oxygen, taken from the oxygen sublattice of the zirconia solid solution, forming CO. This reaction creates oxygen vacancies resulting in a shrinkage of the elementary cell as evidenced by the unit cell parameter measurements of the cubic zirconia phase shown in Fig. 9. A decrease in the cubic cell parameter with the sintering temperature is also observed for the Ca-PSZ material. Two factors are responsible for this: (i) the equilibrium CaO content in the zirconia solid solution decreases with sintering temperature[7] generating a decrease of the cubic cell parameter,[17] (ii) the deviation from stoichiometry (oxygen vacancy concentration) of zirconia at a constant oxygen partial pressure increases with sintering temperature.[18] As shown in Fig. 9, the unit cell parameter of the cubic zirconia phase in the Ca-PSZ/WC composites show an additional decrease due to the WC decomposition. It is worth noticing that the difference of the unit cell parameters, Δ, between the cubic phase in the Ca-PSZ material and the zirconia matrix of the Ca-PSZ/WC composite (Fig. 10) changes with temperature following the changes in the WC and W_2C content (Fig. 3). The Δ value raises when the WC and W_2C decomposition proceeds (up to 1750 °C) and decreases at higher temperature.

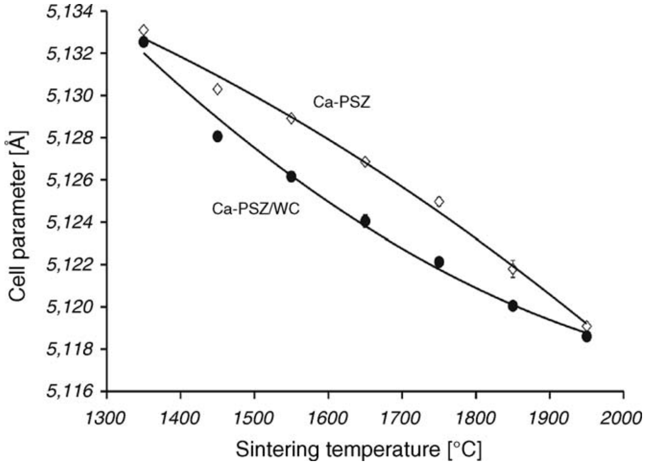

Fig. 9. Unit cell parameter of the cubic zirconia phase in the Ca-PSZ and Ca-PSZ/WC materials as a function of the sintering temperature.

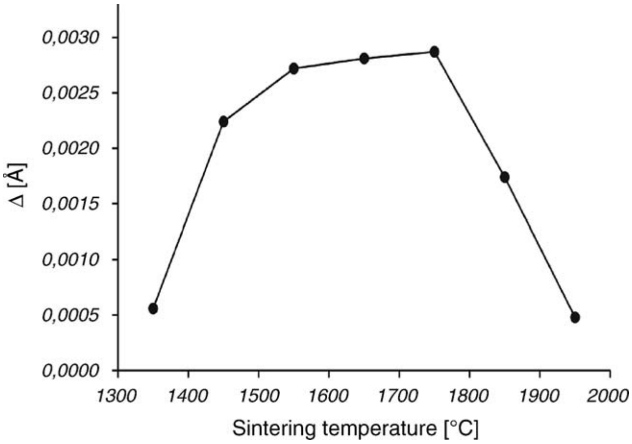

Fig. 10. Unit cell parameter difference, Δ, of the cubic zirconia phase of the Ca-PSZ material and that of the Ca-PSZ/WC composite sintered under the same conditions as a function of the sintering temperature.

The above collected arguments prove that the decomposition of WC creates additional oxygen vacancies according to the following reactions:

$$ZrO_{2-x} + 2yWC = yW_2C + ZrO_{2-x-y} + yCO \quad (1)$$

$$ZrO_{2-x} + yW_2C = 2yW + ZrO_{2-x-y} + yCO \quad (2)$$

with x, the oxygen vacancy concentration in the zirconia matrix connected to the stabilising cation concentration, temperature and sintering atmosphere; y, the oxygen vacancy concentration in zirconia matrix resulting from the WC and W_2C decomposition.

The stability of the cubic and tetragonal polymorphs is known to be critically dependent on the oxygen vacancy concentration in the system.[10,19,20] So, it is not surprising that the increased oxygen vacancy concentration due to the WC decomposition increased the amount of the cubic zirconia in the matrix of the Ca-TZP/WC composites decreasing simultaneously the amount of the tetragonal one (Fig. 2) when compared to the Ca-TZP material.

The presented results clearly indicate that the WC decomposition proceeds without ZrC formation at the temperatures below 1750 °C. This result is different to that obtained in the 3 mol.% Y_2O_3–ZrO_2/WC system where the decomposition of tungsten carbide to metallic tungsten was not observed and ZrC was already found when heat treated at 1500 °C.[1] The differences observed between yttrium and calcium contained system should not be connected to the type of stabilising cation but to other factors influencing the WC decomposition mainly of a kinetic nature, i.e., the size of WC particulates and of a thermodynamic one, i.e., the oxygen vacancy concentration produced by the stabilising oxide. Coincidence of the WC decomposition with zirconia carburisation effects should also be considered.

However, the WC decomposition is accompanied by the ZrC formation above 1750 °C as indicated by the data of Figs. 3 and 4. Some support for this statement comes from thermodynamic calculations[21] showing that ZrC can be formed in the reaction between ZrO_2 and C if the CO partial pressure in the system is lower than 2 atm at 1727 °C and as much as ∼10 atm at 1950 °C.

The relatively poor mechanical properties of the Ca-PSZ/WC composites sintered at high temperatures originate from the small amount of tetragonal ZrO_2 phase and the large amount of cubic zirconia implying a limited amount of transformation toughening and from the porosity due to the WC decomposition process.

5. Conclusions

WC decomposes in calcia-stabilised zirconia matrix during heating at temperatures ranging from 1350 to 1950 °C. The WC decomposition to metallic tungsten proceeds through W_2C and CO formation. Above 1750 °C, the formation of small amounts of ZrC accompanies this process. The WC decomposition changes the cubic and tetragonal zirconia phase contents in the composites through the creation of additional amounts of oxygen vacancies available for the stabilisation process.

The microstructural and phase changes that accompany the incorporation and decomposition of WC improve the mechanical properties of the Ca-PSZ/WC composites sintered above 1650 °C. The W_2C appearance increases the composite hardness in spite of the increased porosity. A bending strength of 417 ± 67 MPa in combination with a hardness of 14.6 ± 0.3 GPa and a fracture toughness of 5.2 ± 0.3 MPa $m^{0.5}$ was measured for the Ca-PSZ/WC composite sintered at 1750 °C. The increased amount of in situ formed metallic tungsten, up to 5.6 vol.% increased the fracture toughness up to 6.8 ± 0.9 MPa $m^{0.5}$ when sintered at 1850 °C. The CO evolved during the WC decomposition limits, however, densification of the Ca-PSZ/WC composites and affects the mechanical properties.

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