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Influence of sintering environment on zirconia–metal carbides characteristics

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Abstract

TaC and TiC powders were added, respectively to a matrix of (CaO + MgO) totally stabilized zirconia and to a CeO_2 stabilized zirconia (PSZ) in order to produce composites by uniaxial pressing. The samples were sintered in vacuum at 1450 °C and in argon environment at 1800 °C, respectively. The purpose of present paper is to establish influence of the type of secondary phase on the mechanical properties of composites and to correlate the physical – mechanical and structural properties of composites with different matrices as function of the amount of secondary phase by varying the TiC and respectively TaC content in 5–30% weight range. Comparative microstructure investigations were made by SEM on sample surfaces. The X-ray diffraction analysis was in accordance with the determined properties of the studied compositions.

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

1. Introduction

Stabilized zirconia policrystalls, as tetragonal polymorph, have an outstanding bending strength (~1000 MPa) and fracture toughness (>10 MPa $m^{1/2}$). These materials have a limited hardness (<1200 kg/mm^2) limiting their use as wear resistant components. On the other hand, pure carbide inclusions have an excellent hardness,[1–4] but a limited bending strength, fracture toughness and stiffness.[4,5] The degree of improvement is in different ZrO_2–TiX (X = C, B_2, N, CN) composite systems.[6,7]

To combine the excellent properties of stabilized zirconia with the increased hardness obtainable by incorporation of a secondary phase such as TaC or TiC was the main objective of this work. The influence of sintering environment (vacuum at 1450 °C and in argon at 1800 °C) on mechanical strength and microstructure changes – of composites obtained from (CaO + MgO) stabilized zirconia (CaMg-SZ) and CeO_2 stabilized zirconia (Ce-SZ), respectively by adding the mentioned carbide inclusions – was investigated.

2. Experimental procedure

2.1. Starting materials

2.1.1. CaO and MgO stabilized zirconia matrix

In a (3% CaO + 1% MgO) stabilized zirconia (PSZ) matrix TiC or TaC powder in a proportion of 5–30% by weight was dispersed.

2.1.2. In situ CeO_2 stabilized zirconia matrix

A 92:8 ratio (by weight) of unstabilized (monoclinic) ZrO_2 and CeO_2 powders mixture was prepared. The carbides powders were added to the zirconia matrix mixed and homogenised in an attritor with isopropyl alcohol using zirconia balls, for 2 h. In zirconia matrices TiC and TaC powder, respectively were dispersed, in a proportion of 5–30% by weight. The raw materials characteristics are summarised in Table 1. The particles size distribution of the powders was determined by using a laser grains size Fritsch tester (dm) and the Fischer method (d50)[5] (see Table 1).

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Table 1
Characteristics of raw materials

Raw material	Chemical composition	Mineralogical phase	d50[a] (μm)	dm[b] (μm)
Stabilized zirconia	Min. 94.5.5% $ZrO_2 + HfO_2$	Cubic ZrO_2	3.17	3.2
Unstabilized zirconia	Min. 99.5% ZrO_2	Monoclinic ZrO_2	0.9	0.92
Ceria oxide	Min. 99.9% CeO_2	Cubic CeO_2	0.23	0.25
Titanium carbide	Min. 98.0% TiC	Cubic TiC	2.8	2.5
Tantalum carbide	Min. 98.0% TaC	Cubic TaC	0.8	0.82

[a] d50: the average size determined by Fischer method.

[b] dm: the median diameter determined by laser granulometry.

2.2. *Fabrication and sintering*

The batches were pressed as plates (10 mm × 10 mm × 10 mm) and sintered at 1450 °C in vacuum (at 10^{-4} Torr) in a Baltzers type kiln, the treatment corresponding to a rapid diagram (6 h). The same samples were treated at 1800 °C in argon environment. Batches with CaMg-SZ + TiC and Ce-SZ + TiC compositions were prepared as given in Table 2.

2.3. *Mechanical properties*

The bending strength at room temperature was measured on a MTS machine under 100KN testing load on parallelepipeds with dimensions of 5 mm × 5 mm × 50 mm.

The microindentation technique, with a load of 2500 g (applied for 15 s) was employed to measure the Vickers hardness (H_V) by using a Shimadzu Seisakusho Ltd. device.

2.4. *Microstructure*

A TUR – 4 diffractometer with Cu Kα radiation was used to record the mineralogical transformations after sintering. Microstructure and grain size studies were performed through Scanning Electron Microscopy (SEM) a Hitachi S2600N device.

3. Results and discussions

3.1. *Mechanical properties – bending strength and Vickers hardness*

The influence of the TiC content after sintering in vacuum at 1450 °C and in argon at 1800 °C on bending strengths of the two ZrO_2 matrices composites are represented in Fig. 1a and b. The bending strengths developed in argon by the Ce-stabilized zirconia matrix composites are higher than those of stabilized Ca-Mg-stabilized zirconia matrix composites for all considered compositional range. The bending strengths of the same samples sintered in argon at 1800 °C decreases with the increasing of TiC amount (from 5% to 30%) – Fig. 1b. The samples with Ce-ZrO_2 matrix sintered in vacuum at 1450 °C – Fig. 1b have an opposite behaviour of bending strengths which increases with the added TiC content.

The influence of the TaC content after sintering in vacuum at 1450 °C and in argon at 1800 °C on bending strength of the both ZrO_2 matrices composites are shown in Fig. 2a and b. The

Table 2
Composition of zirconias–carbides composites

Specimens	Stabilized zirconia (wt.%)	Cerium oxide (wt.%)	Titanium carbide (wt.%)	Tantalum carbide (wt.%)
With CaO + MgO-stabilized zirconia matrix				
5Ti-CMZ	95	–	5	–
10Ti-CMZ	90	–	10	–
20Ti-CMZ	80	–	20	–
30Ti-CMZ	70	–	30	–
5Ta-CMZ	95	–	–	5
10Ta-CMZ	90	–	–	10
20Ta-CMZ	80	–	–	20
30Ta-CMZ	70	–	–	30

Specimens	Monoclinic zirconia (wt.%)	Cerium Oxide (wt.%)	Titanium Carbide (wt.%)	Tantalum Carbide (wt.%)
With CeO_2 stabilized zirconia matrix				
5Ti-CeZ	87.4	7.6	5	–
10Ti-CeZ	82.8	7.2	10	–
20Ti-CeZ	73.6	6.4	20	–
30Ti-CeZ	64.4	5.6	30	–
5Ta-CeZ	95	–	–	5
10Ta-CeZ				
20Ta-CeZ				
30Ta-CeZ				

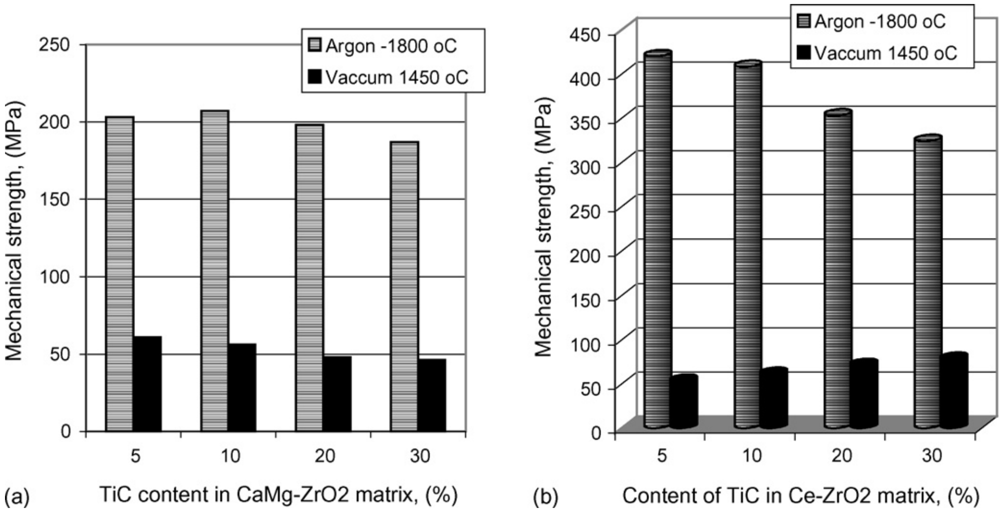

Fig. 1. Evolution of bending strength of Ca + Mg-stabilized ZrO_2 and of e-stabilized ZrO_2 vs. TiC content, after sintering in vacuum at 1450 °C (a) and after sintering at 1800 °C in argon environment (b).

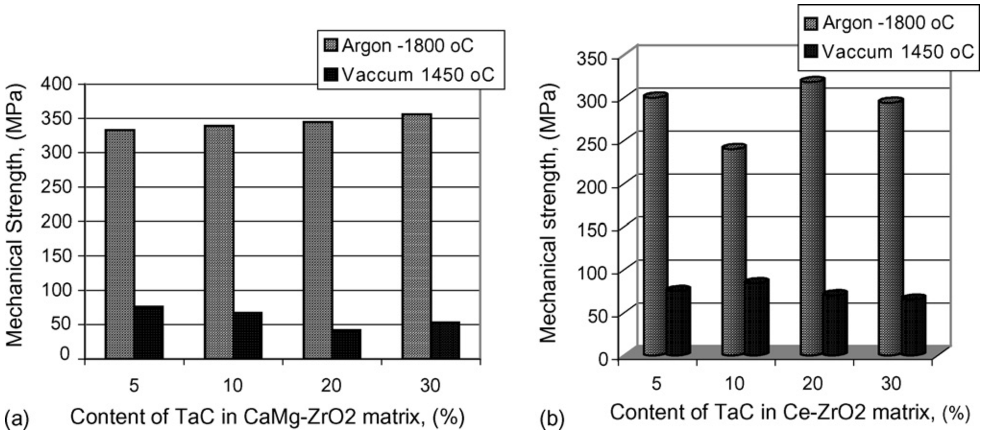

Fig. 2. Evolution of bending strength of Ca + Mg-stabilized ZrO_2 and of Ce-stabilized ZrO_2 vs. TaC content, after sintering in vacuum at 1450 °C (a) and after sintering at 1800 °C in argon environment (b).

best bending strength developed in argon by the Ce-stabilized zirconia matrix composites is corresponding to the addition of 20% TaC. The same composition samples sintered in vacuum at 1450 °C – Fig. 2b have an opposite behaviour of bending strengths which decreases with the added TaC content.

The bending strengths of Ca-Mg-stabilized zirconia matrix composites treated in argon at 1800 °C and in vacuum at 1450 °C show a little variation as function as the TaC content increases – Fig. 2a.

Comparing the influence of the nature of the added carbides on mechanical strengths – Figs. 1a and b and 2a and b should be noticed that TiC seems to lead to better results for the Ce-stabilized zirconia matrix.

Microindentation technique, was employed to measure the Vickers hardness for selected specimens of $Ce\text{-}ZrO_2$ matrix with TiC and TaC fired in vacuum at 1450 °C and in argon at 1800 °C, respectively, the results are plotted in Figs. 3 and 4. It results that the hardness increases with increasing of carbides content and the addition of TiC – Fig. 3 leads to highest hardness comparatively with TaC addition – Fig. 4 in both considered firing conditions.

3.2. Microstructure

The XRD analysis results of some selected composites with TiC inclusions (5Ti-CMZ, 20Ti-CMZ, 5Ti-CeZ and 20Ti-CeZ) are given in Table 3. The composites sintered in argon at

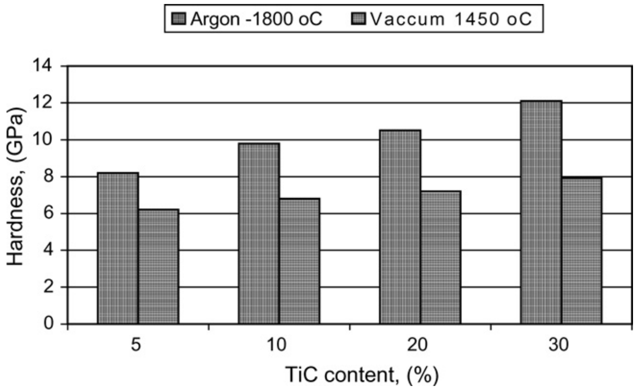

Fig. 3. Evolution of Vickers hardness (Hv) of Ce-stabilized ZrO_2 matrix with TiC content, after sintering in argon at 1800 °C and in vacuum at 1450 °C, respectively.

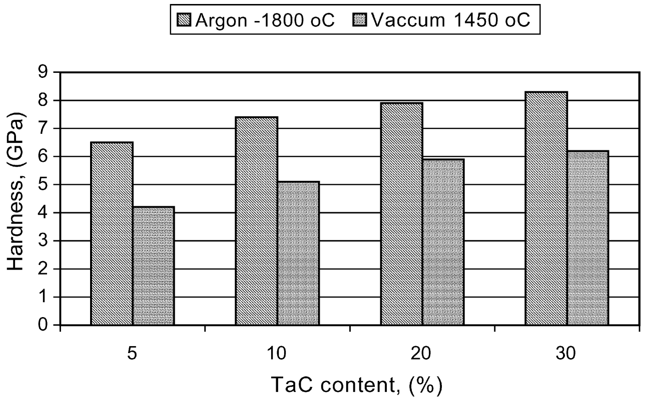

Fig. 4. Evolution of Vickers hardness (Hv) of Ce-stabilized ZrO_2 matrix with TaC content, after sintering in argon at 1800 °C and in vacuum at 1450 °C, respectively.

Table 4
Crystalline phases in CaMg-SZ + TaC and Ce-SZ + TaC composites

	C-ZrO_2	T-ZrO_2	M-ZrO_2	TaC	CeO_2
Fired at 1800 °C in argon					
5Ta-CMZ	a			b	
20Ta-CMZ	a			c	
5Ta-CeZ	b	c	a	b	
20Ta-CeZ	c	b	a	b	
Fired at 1450 °C in vacuum					
5Ta-CMZ	a			b	
20Ta-CMZ	a			c	
5Ta-CeZ		c	a	b	b
20Ta-CeZ		c	a	c	b

Where C: cubic, T: tetragonal, and M: monoclinic.
[a] High content.
[b] Low content.
[c] Medium content.

1800 °C realized with Ca-Mg-stabilized zirconia consist mainly of cubic zirconia and cubic TiC and this could explain the lower mechanical strengths, instead of the composites obtained with Ce-stabilized zirconia which consists in a mixture of tetragonal zirconia, monoclinic zirconia and cubic TiC. The samples fired in vacuum at 1450 °C present the same mineral compounds, but the amount of monoclinic polymorph is higher and some unreacted CeO_2 was detected in the 20Ti-CeZ composite. This mineralogical composition could explain the mechanical weakness of composites sintered in vacuum at 1450 °C.

The XRD analysis results of some selected composites with TaC inclusions (5Ta-CMZ, 20Ta-CMZ, 5Ta-CeZ and 20Ta-CeZ) are given in Table 4. The composites sintered in argon at 1800 °C realized with Ca-Mg-stabilized zirconia consist mainly of cubic zirconia and cubic TaC. The composites with Ce-stabilized zirconia matrix fired in the same conditions are a mixture of minor cubic zirconia, tetragonal zirconia, and major monoclinic zirconia and cubic TaC.

The 5Ta-CMZ and 20Ta-CMZ composites fired in vacuum at 1450 °C present mainly cubic zirconia and TaC. A major amount of monoclinic zirconia were detected in 5Ta-CeZ and 20Ta-CeZ composites associated with tetragonal zirconia and unreacted CeO_2.

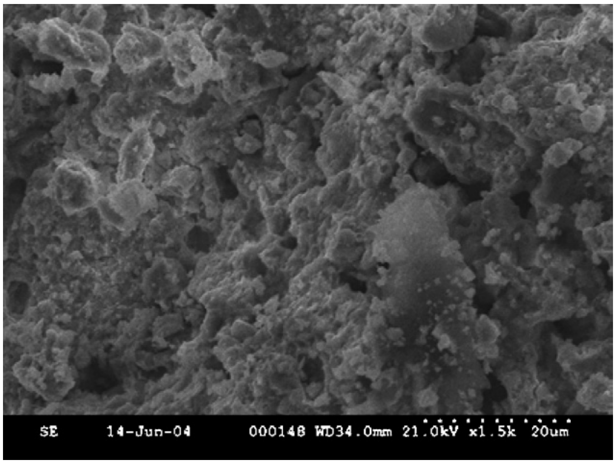

Fig. 5. SEM micrograph of 20Ti-CeZ composite fired in argon at 1800 °C.

Microstructural evidences on 20Ti-CeZ composite fired in argon at 1800 °C – Fig. 5 and fired in vacuum at 1450 °C – Fig. 6 have suggested that the TiC inclusions (20 wt.%) were

Table 3
Crystalline phases in CaMg-SZ + TiC and Ce-SZ + TiC composites

	C-ZrO_2	T-ZrO_2	M-ZrO_2	C-TiC	CeO_2
Fired at 1800 °C in argon					
5Ti-CMZ	a			b	
20Ti-CMZ	a			c	
5Ti-CeZ		c	a	b	
20Ti-CeZ		a	c	c	
Fired at 1450 °C in vacuum					
5Ti-CMZ	a		c	b	
20Ti-CMZ	a			c	
5Ti-CeZ		c	a	b	
20Ti-CeZ		c	a	c	d

Where C: cubic, T: tetragonal, and M: monoclinic.
[a] High content.
[b] Low content.
[c] Medium content.
[d] Trace at XRD detection limit.

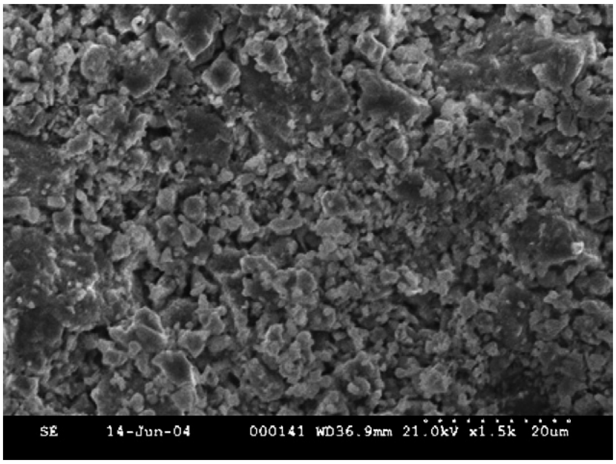

Fig. 6. SEM micrograph of 20Ti-CeZ composite fired in vacuum at 1450 °C.

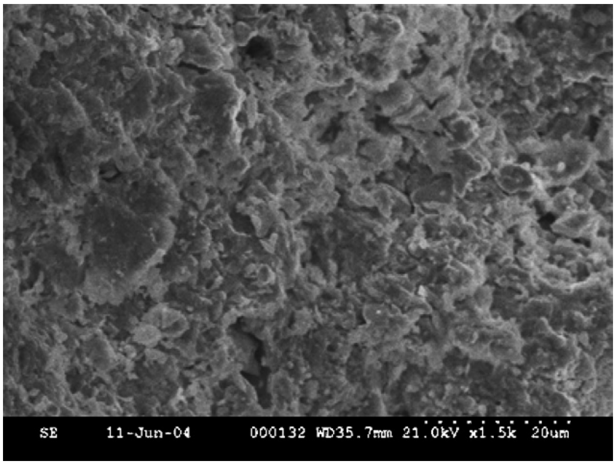

Fig. 7. SEM micrograph of 20Ta-CeZ composite fired in argon at 1800 °C.

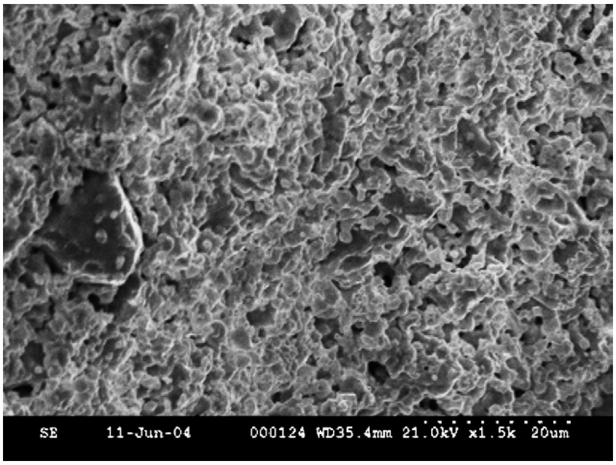

Fig. 8. SEM micrograph of 20Ta-CeZ composite fired in vacuum at 1450 °C.

sufficiently mobile at 1800 °C, in argon to move with the grain junctions and eventually coalesce at grain boundary. The information and observation concerning carbide inclusions in ZrO_2 matrix assess the role of grain growth on voids trapped within grains during the last stage of sintering.

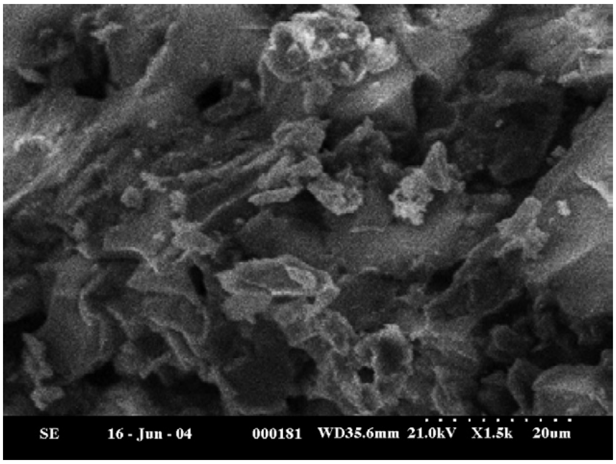

Fig. 9. SEM micrograph of 20Ti-CMZ composite fired in argon at 1800 °C.

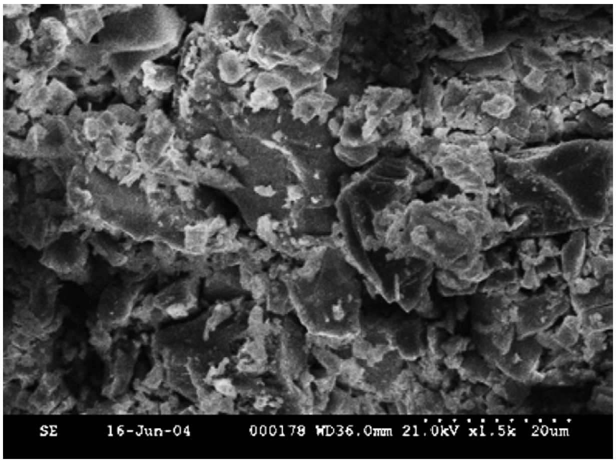

Fig. 10. SEM micrograph of 20Ti-CMZ composite fired in vacuum at 1450 °C.

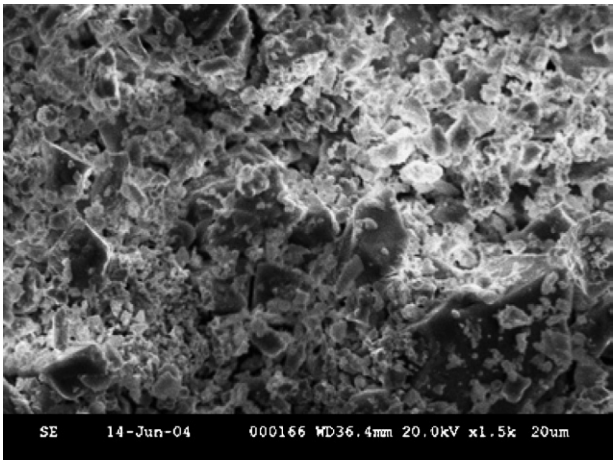

Fig. 11. SEM micrograph of 20Ta-CMZ composite fired in argon at 1800 °C.

Voids are trapped inside the grains during sintering because their mobility is insufficient relative to that of grain boundaries, i.e. analogous to the Al_2O_3 inclusions in ZrO_2 at temperatures above 1600 °C.[8,9]

Microstructural evidences on 20Ta-CeZ composite fired in argon at 1800 °C is given in Fig. 7 and on specimens

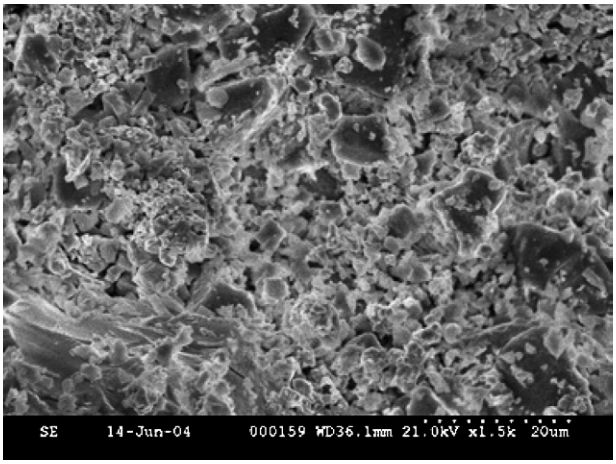

Fig. 12. SEM micrograph of 20Ta-CMZ composite fired in vacuum at 1450 °C.

with TaC inclusions (20 wt.%) fired in vacuum at 1450 °C in Fig. 8.

The microstructural arrangement in a 20Ti-CMZ composite, fired in argon at 1800 °C is illustrated in Fig. 9, that of a specimen with TiC inclusions (20 wt.%) fired in vacuum at 1450 °C is shown in Fig. 10.

The microstructure of a 20Ta-CMZ composite, fired in argon at 1800 °C is shown in Fig. 11, respectively, that of a specimen with fired in vacuum at 1450 °C in Fig. 12 with TaC inclusions (20 wt.%). The grain growth in a 20Ti-CMZ composite (Fig. 9), in argon environment is enhanced (~10 μm) comparatively with the same content TiC composites in Ce-stabilized matrix, where the average grain size is ~3,5 μm).

4. Conclusions

Argon environment sintering at 1800 °C was effective to prepare two types of composites based on a matrix of (CaO + MgO) stabilized zirconia and CeO_2 stabilized zirconia, respectively, in which TiC and TaC were dispersed by solid state reactions.

The best bending strength and hardness were developed by the CeO_2 stabilized zirconia matrix composites with TiC inclusions.

The firing in vacuum, at 1450 °C, of both stabilized zirconia matrices with TiC and TaC was insufficient to develop improved mechanical strengths composites.

The fracture toughness of ZrO_2-TiC and ZrO_2-TaC composite is strongly influenced by microstructure mainly by the presence of tetragonal precipitation zirconia.

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References

1. Dingh, Zh., Oberacker, R. and Thumler, F., *J. Eur. Ceram. Soc.*, 1993, **12**, 377.
2. Haberko, K., Pedzich, Z., Rog, G., Bucko, M. M., Faryna, M. and Kowal, A., *Eur. J. Solid State Inorg. Chem.*, 1995, **32**, 593.
3. Poorterman, M., Descams, P., Cambier, F., Leriche, E. and Thierry, B., *J. Eur. Ceram. Soc.*, 1993, **12**, 103.
4. Pedzich, Z., Haberko, K., Pierkarczyk, J., Faryna, M. and Litynska, L., *Mater. Lett.*, 1998, **36**(7), 70.
5. Volceanov, E., Motoc, Ş., Volceanov, A., Neagu, R. and Coman, C., *Development of ZrO_2/ZTA/TiC Composites, Key Engineering Materials 264–266 Trans*. Tech Publications, Switzerland, 2004, pp. 2283–2286.
6. Veugels, J. and Van Der Biest, O., *ZrO_2 – TiX Composites, Key Engineering Materials 132–136 Trans*. Tech Publications, Switzerland, 2004, p. 2064.
7. Shoubu, K., Watanabe, T., Drennan, J., Hannink, R. and Swain, M., *Science and Technology of Zirconia III, Vol 24*, Proceedings of the Fourth International Conference on the Science and Technology of Zirconia, Tokyo, Am. Ceram. Soc., Columbus, Ohio, 1986, p. 1091.
8. Lange, F. F. and Hirlinger, M. M., Grain growth in two-phase ceramics: Al_2O_3 inclusions in ZrO_2. *J. Am. Ceram. Soc.*, 1987, **70**(11), 827–830.
9. Lange, F. F. and Hirlinger, M. M., Hindrance of grain growth in Al_2O_3 by ZrO_2 inclusions. *J. Am. Ceram. Soc.*, 1984, **67**(3), 164–168.