Effect of carbon treatment on surface hardening of TiY–TZP

K. Haberko[a],*, A. Wajler[a], M.M. Bućko[a], Z. Pędzich[a], M. Faryna[b], W. Pyda[a],
J. Piekarczyk[a]

[a]University of Mining and Metallurgy, Faculty of Materials Science and Ceramics, Al.Mickiewicza 30, 30-059 Cracow, Poland
[b]Institute of Metallurgy and Materials Science, Polish Academy of Sciences, ul. Reymonta 25, 30-059 Cracow, Poland

Abstract

A powder of TiO_2–Y_2O_3–ZrO_2 solid solution was prepared by the coprecipitation-calcination technique. Its sintering at 1400 °C lead to the dense material composed mostly of the tetragonal symmetry phase. Samples of these material were inserted into a carbon bed and heat treated at 1650 °C in Ar atmosphere. Titanium carbide inclusions in the form of elongated particles were precipitated in the near surface layer of the material. Its surface hardness increased essentially. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. Inclusions; D. ZrO_2; Surface hardness; Titanium carbide

1. Introduction

Tetragonal zirconia polycrystals (TZP) show high fracture toughness but relatively low hardness of these materials limits their potential applications. Numerous investigations proved that carbide inclusions and inclusions of chromia particles in the TZP matrix resulted in the materials of higher hardness and fracture toughness [1–8]. The inclusions were introduced by the physical mixing of the starting powders or by growing such inclusions due to the reaction of the zirconia solid solution powder with carbon. The latter possibility is exemplified by the TZP–TiC system [9]. In this case titanium carbide was synthesised by the reaction of the nanometric TiO_2–Y_2O_3–ZrO_2 solid solution powder with evenly distributed carbon derived from the pyrolysis of phenol-formaldehyde resin.

It will be shown in the present paper that a hard surface layer results from the reaction of the dense polycrystalline solid solution material in the TiO_2–Y_2O_3–ZrO_2 system with carbon.

2. Experimental procedure

The solid solution powder in the TiO_2–Y_2O_3–ZrO_2 system was prepared by the coprecipitation-calcination technique. To do this the water solution of $TiCl_4$, YCl_3 and $ZrOCl_2$ was introduced into a vigorously stirred NH_3 solution. Final pH = 9 of the suspension was sufficient to lead to the quantitative precipitation of the constituent elements. The X-ray amorphous gel was washed with distilled water to remove NH_4Cl then dried and calcined at 1000 °C for 1 h. The resulting solid solution corresponded to 18 mol% TiO_2, 3 mol% Y_2O_3 and 79 mol% ZrO_2 contents. According to our previous investigations [10–12], a solid solution of such composition should result in the polycrystalline material in which the phase of tetragonal symmetry dominates. Specific surface area 9 m^2/g, as measured by the nitrogen adsorption, resulted from the attrition grinding with the 2 mm Y-TZP balls. The powder was uniaxially compacted under 50 MPa. Rectangular tiles of 60 × 70 × 7 mm size were isostatically repressed under 200 MPa and air sintered for 2 h at 1400 °C. Bars of approximate sizes of 5 × 5 × 45 mm were prepared by cutting the tiles with a diamond saw. Then they were polished using diamond pastes, the final one of grain sizes <1 μm. Some bar samples were additionally heat-treated for 2 h at 1650 °C in air atmosphere.

* Corresponding author.
E-mail address: haberko@uci.agh.edu.pl (K. Haberko).

The bars air-sintered at 1400 °C were inserted into a powder composed of graphite (60 wt.%) and phenol-formaldehyde resin (40 wt.%). A two-stage thermal treatment in argon atmosphere was applied. At lower temperature (800 °C) the samples were covered with carbon due to the pyrolysis of resin. The final treatment was performed for 2 h at 1650 °C in the furnace equipped with the graphite heating element.

3. Results and discussion

3.1. Phase composition

Fig. 1 shows X-ray diffraction pattern taken from the surface of the starting material air-sintered for 2 h at 1400 °C (A), the material was subjected to reaction with carbon for 2 h at 1650 °C (C). The diffraction pattern of the sample (A) additionally treated for 2 h in air at 1650 °C is illustrated in Fig. 1B. The phase of tetragonal symmetry dominates in the samples heat-treated in air (A and B). Certain amounts of the cubic phase are also visible. Based on the X-ray diffraction patterns, proportions of these phases were determined by the Rietveld method [13–15]. They are presented in Table 1.

Data of Table 1 indicate an increasing fraction of the cubic phase with the temperature of heat treatment in air atmosphere. Such a behaviour is usually observed in the numerous zirconia s.s. systems. An essential composition change can be noticed, however, in the case of the material subjected to the surface reaction with carbon in an oxygen free atmosphere (Fig. 1C). In this sample only cubic zirconia s.s. polymorph occurs. Comparing this fact with the sample B, heat treated at

the same temperature but in the air atmosphere, we conclude that de-oxidation of the system seems to be the plausible reason of the cubic phase formation. Initially ivory colour of the samples sintered in air turns to black colour in case of the material subjected to the carbon treatment in oxygen free atmosphere. This fact indicates oxygen deficit in the system [16]. Its stabilizing effect for the high symmetry cubic zirconia phase was observed in our earlier works [17,18] and in the low-oxygen part of the zirconium—oxygen system [19]. According to [20] the enhanced level of concentration of oxygen vacancies is the factor responsible for this effect. This concentration should be increased under the oxygen-free heat treatment conditions. A system specially susceptible to such a behaviour should be the one containing titanium because of the flexible valency of this element; reduction of Ti^{+4} to Ti^{+3} or even Ti^{+2} has to result in the increased concentration of oxygen vacancies in the zirconia solid solution. Cubic symmetry zirconia was indeed observed in the ZrO_2–TiO_2 solid solution material sintered in argon atmosphere [18]; the same sample sintered in air was monoclinic.

In Fig. 1C three reflections attributed to titanium carbide, (111), (200) and (220), occur in the sample heat-treated in contact with carbon. Based on these reflections the lattice parameter of this carbide was assessed.

Table 1
Content of zirconia polymorphs measured on the sample surfaces. Heat treatment conditions indicated

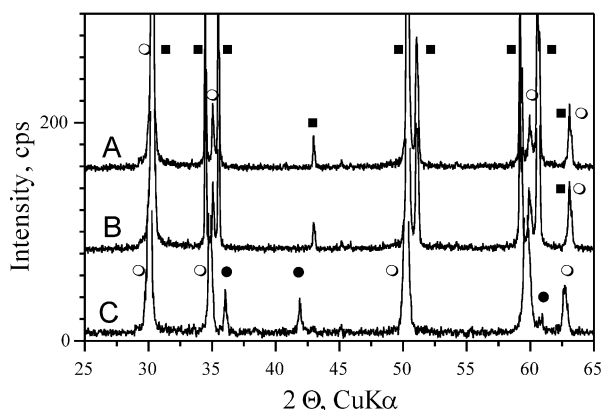| Temperature of heat treatment	Tetragonal phase	Cubic phase
1400 °C (air)	80.9 wt.%	19.1 wt.%
1650 °C (air)	72.4 wt.%	27.6 wt.%
1650 °C (Ar + C)	–	100 wt.%

Fig. 1. X-ray diffraction patterns taken from the sample surfaces (CuK$_\alpha$): A – material air sintered for 2 h at 1400 °C, B – sample A additionally heat treated in air for 2 h at 1650 °C, C – material air sintered for 2 h at 1400 °C and then reacted with carbon at 1650 °C in Ar atmosphere. ■—zirconia s.s of tetragonal symmetry, ○—zirconia s.s of cubic symmetry, ●—titanium carbide.
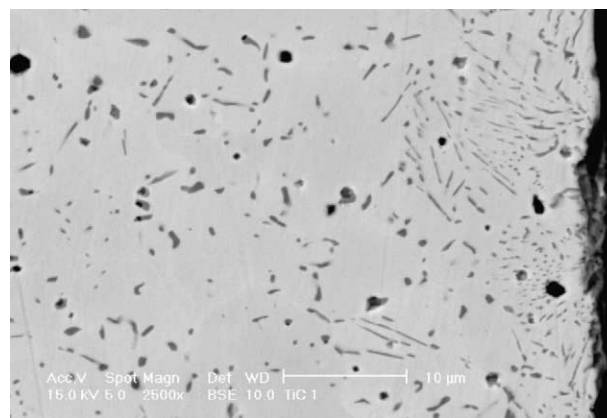

Fig. 2. Cross-section through the surface layer of the sample subjected to the carbon treatment (SEM back scattered electrons).

It equals the 0.4303 nm. Using the relation of the titanium carbide lattice parameter vs. carbon content [21] we find that this compound corresponds to the formula characterised by a large carbon deficit, $TiC_{0.47}$.

The cross-section through the material perpendicular to its surface (Fig. 2) reveals precipitates that have the form of thin (about 100 nm) elongated particles. Their concentration decreases with the distance from the surface. No inclusions were observed when distance from the surface was greater than about 160 μm. Line analysis (EDS) shown in Fig. 3 indicate increased Ti concentration within the inclusions. Results of the X-ray diffraction (Fig. 1) and chemical analysis of Fig. 3 give a strong premise for the phase composition of the inclusions; they correspond to titanium carbide.

3.2. Properties

In Table 2 Vickers hardness (HV) measured under 10 G load on the slightly polished surface of the sample, three point bending strength (σ), Modulus of elasticity
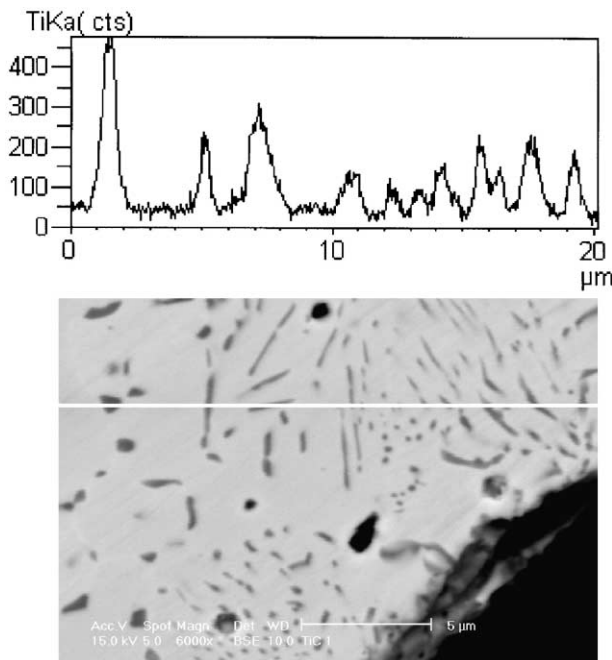

Fig. 3. Distribution of Ti along the indicated line.

(E) measured by the ultrasonic method [22] in the direction perpendicular to the sample surface and bulk density (d) are shown. These data demonstrate that surface reaction with carbon changes properties of the material. The decreased strength of the material should be attributed most probably to the transformation of the initially tetragonal phase to the cubic one. Now it is well established that the martensitic transformation of the tetragonal phase to the monoclinic symmetry one in front the crack tip advancing through the material is the source of its high fracture toughness and also high strength. So, the zirconia material lacking a tetragonal phase should show lower strength, which is really the case.

Elastic properties of the samples heat-treated in air at 1400 °C and additionally also in air at 1650 °C do not differ, as is demonstrated by the Young moduli values (Table 2). It confirms the mentioned above fact (see Table 1) that no essential phase changes occur at higher heat treatment temperature and that densities of the sample are comparable (see Table 2). Essentially higher moduli of elasticity are, however, observed in the material subjected to the surface reaction with carbon. But it cannot be attributed to the surface layer containing titanium carbide inclusions. This conclusion is justified by the statistically not valid difference of the E values observed in the same sample with the removed 200 μm surface layer. Most probably the near surface layer, in which the concentration of carbide inclusions decreases towards the sample centre, is too thin to influence elastic properties of the whole material significantly. So, it can be concluded that de-oxidation of the sample and a deep change of its phase composition related to it, leads to the more rigid material.

Data of Table 2 indicate that a reaction with carbon results in the pronounced increase of the sample surface hardness. It was also measured on the cross section through the sample. Fig. 4 shows changes of hardness vs. distance from the surface. The lest square straight line relationship gives a high correlation coefficient $|r| = |0.810|$ which is much higher than its critical value at a confidence level of 0.999 ($r_{crit} = 0.519$). The slope ratio at the same confidence level is essentially different from zero. These facts prove that the surface layer, containing carbide inclusions, is harder than the underlying material.

Table 2
Properties of the samples

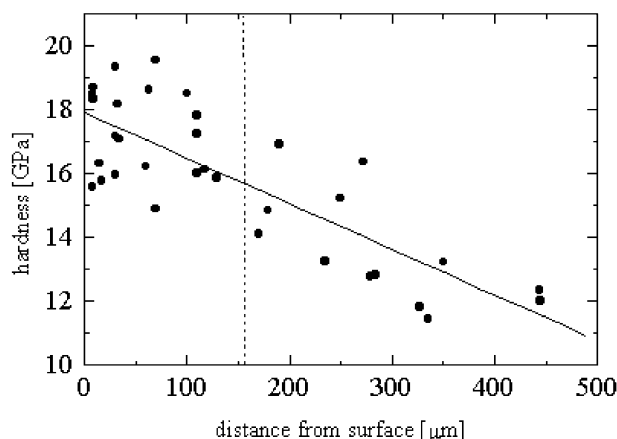| Sample – preparation conditions	HV (GPa)	σ (MPa)	E (GPa)	d (g/cm³)
1400 °C (air)	10.5±1.1	426±83	156.0±6.5	5.722±0.009
1650 °C (air)	11.0±1.6	–	157.3±5.8	5.723±0.010
1650 °C (Ar+C)	18.3±1.0	193±83	213.3±10.5	5.721±0.012
1650 °C (Ar+C, surface layer removed)	15.3±1.5	–	214.2±9.5	5.733±0.011

±Confidence interval at confidence level of 0.95.

Fig. 4. Vickers hardness (10 G load) vs. distance from the surface. The dashed line indicates thickness of the area with TiC_{1-x} inclusions.

4. Summary and conclusions

- Titanium carbide characterized by the carbon deficit results from the surface reaction of dense TiY–TZP with carbon.
- Inclusions of TiC_{047} present in the near-surface layer of the sample have the form of elongated particles distributed within the cubic zirconia matrix.
- Titanium carbide inclusions are responsible for the increased hardness of the TiY–TZP sample surface.
- Initially tetragonal symmetry zirconia solid solution transforms to the cubic symmetry during the high temperature treatment in the oxygen free atmosphere. This is due to the partial de-oxidation of the system and the increased yttria concentration.
- Mechanical strength of the system is reduced due to its transformation to cubic symmetry.

References

[1] N. Claussen, K.L. Weisskopf, M. Rühle, Tetragonal zirconia polycrystals reinforced with SiC whiskers, J. Am. Ceram. Soc. 68 (1986) 288–292.

[2] G.Y. Lin, T.C. Lei, S.X. Wang, Y. Zhou, Microstructure and mechanical properties of SiC whiskers reinforces ZrO_2 (2% mol. ZrO_2), Ceram. Int. 22 (1996) 199–205.

[3] M. Poorteman, P. Descamps, F. Cambier, J. Leriche, B. Thierry, Hot isostatic pressing of SiC platelets/Y-TZP, J. Eur. Ceram. Soc. 12 (1993) 103–109.

[4] Zh. Ding, R. Oberacker, F. Thümmler, Microstructure and mechanical properties of yttria stabilized tetragonal zirconia polycrystals (Y-TZP) containing dispersed silicon carbide particles, J. Eur. Ceram. Soc. 12 (1993) 377–383.

[5] K. Haberko, Z. Pędzich, G. Róg, M.M. Bućko, M. Faryna, The TZP Matrix–WC particulate composites, Eur. J. Solid State Inorg. Chem. 32 (1995) 593–601.

[6] Z. Pędzich, K. Haberko, J. Piekarczyk, M. Faryna, L. Lityńska, Zirconia matrix–tungsten carbide particulate composites manufactured by hot-pressing technique, Mater. Lett. 36 (1998) 70–75.

[7] Z. Pędzich, K. Haberko, J. Babiarz, M. Faryna, The TZP–chromium oxide and chromium carbide composites, J. Eur. Ceram. Soc. 18 (1998) 1939–1944.

[8] K. Haberko, Z. Pędzich, J. Dutkiewicz, M. Faryna, A. Kowal, Microstructure of the particulate composites in the (Y)TZP–WC system, in: A.P. Tomsia, A.M. Gleaser (Eds.), Ceramic Microstructures: Control at the Atomic Level, Plenum Press, New York, 1998, pp. 741–748.

[9] K. Haberko, W. Pyda, Z. Pędzich, M.M. Bućko, A TZP matrix composite with the in situ grown TiC inclusions, J. Eur. Ceram. Soc. 20 (2000) 2649–2654.

[10] K. Haberko, W. Pyda, M.M. Bućko, M. Faryna, Tough materials in the system TiO_2–Y_2O_3–ZrO_2, in: G. Ziegler, H. Hausner (Eds.), Euro-Ceramics II Proceedings, vol. 2 Structural Ceramics and Composites, Deutsche Keramische Gesellschaft, Koln, 1991, pp. 957–961.

[11] W. Pyda, K. Haberko, M.M. Bućko, M. Faryna, A study on preparation of tetragonal polycrystals (TZP) in the TiO_2–Y_2O_3–ZrO_2 system, Ceram. Int. 18 (1992) 321–326.

[12] W. Pyda, K. Haberko, M.M. Bućko, M. Faryna, TZP in the TiO_2–Y_2O_3–ZrO_2 system, in: S.P.S. Badwal, M.J. Bannister, R.H.J. Hannink (Eds.), Science and Technology of Zirconia V, Technomic Publishing Co. Inc., Lancaster, Pennsylvania, 1993, pp. 136–143.

[13] H.M. Rietveld, Line profiles for neutron powder diffraction peaks for structure refinement, Acta Crystallogr. 22 (1967) 151.

[14] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2 (1969) 65.

[15] R.A. Young, A. Sakthiel, T.S. Moss, C.O. Paiva-Santos, DBWS-9411 an upgrade of the D.B.W.S. programs for Rietveld refinement with PC and mainframe computers, J. Appl. Crystallogr. 28 (1995) 366.

[16] S.C. Carniglia, S.D. Brown, T.F. Schroeder, Phase equilibria and physical properties of oxygen-deficient zirconia and thoria, J. Am. Ceram. Soc. 54 (1971) 13–17.

[17] K. Haberko, W. Pyda, J. Piekarczyk, M.M. Bućko, Effect of carbon reduction on properties of the 13 mol% TiO_2–3 mol% Y_2O_3–84 mol% ZrO_2, J. Am. Ceram. Soc. 75 (1992) 1272–1275.

[18] K. Haberko, W. Pyda, Z. Pędzich, M.M. Bućko, Tetragonal zirconia polycrystals under reducing conditions, in: P. Duran, J.F. Fernandez (Eds.), Third Euro-Ceramics, vol. 1 Processing of Ceramics, Faenza Editrice Iberica, Madrid, 1993, pp. 967–972.

[19] R. Ruh, H.J. Garrett, Nonstoichiometry of ZrO_2 and its relation to tetragonal-cubic inversion in ZrO_2, J. Am. Ceram. Soc. 50 (1967) 257–261.

[20] P. Kountouros, G. Petzow, Defect chemistry, phase stability and properties of zirconia polycrystals, in: Science and Technology of Zirconia V, Technomic Publishing Co. Inc, Lancaster, PA, 1993, pp. 30–48.

[21] J. Walter, PhD thesis, University of Technology, Cracow, Poland, 1999.

[22] J. Piekarczyk, H. Hennicke, R. Pampuch, On determining the elastic constants of porous zinc ferrite materials, Ceram. Forum Int./Ber.DKG 59 (1982) 227–232.