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Effect of sintering environment on the structure of calcia-stabilised TiO_2-added zirconia solid solutions

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Abstract

Four sets of calcium-stabilised TiO_2-added zirconia polycrystals were produced to study the response of zirconia structure to the sintering environment. Two sample sets originated from pressureless sintering of the zirconia powders in air and argon, respectively. In the third set, the zirconia powders were hot-pressed in argon in the unavoidable contact with the graphite foil. The set forth differed from the third one in the presence of WC particulates. Rietveld refinements with X-ray diffraction data were used to determine the phase composition of the sintered bodies and unit cell volumes of zirconia polymorphs. It was found that deoxidation of the calcia-stabilised zirconia solid solutions at 1200–1350 °C is a weak factor for the tetragonal phase content increase. The TiO_2 incorporation inhibited deoxidation and decreased the amount of tetragonal polymorph. The importance of additional oxygen vacancies and residual stresses for the stabilisation of tetragonal zirconia was discussed.

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1. Introduction

The sintering environment plays an important role in the production of many materials influencing the final properties obtained. This concerns also the zirconia based materials finding widespread use. Due to the close relationship between the oxygen partial pressure and zirconia stoichiometry, the sintering atmosphere controls the phase composition both of pure and stabilised zirconia.[1] However, the zirconia stoichiometry can be influenced not only by the sintering atmosphere of different oxygen partial pressure but also by any reaction which consumes or creates oxygen vacancies, e.g. intentional or unintentional carburisation combined with the carbon-alloying dopant reaction,[2] chemical reaction between reinforcement and zirconia particles,[3] etc. Such a reaction, which can accompany the sintering process of the zirconia based body, together with the sintering atmosphere, creates the sintering environment contributing to the resultant properties. In such a meaning, the concept of sintering environment is applied in this work dealing with the calcia-stabilised TiO_2-added zirconia solid solutions, embedded in different environments.

The materials based on the zirconia solid solutions under consideration are difficult to obtain if the majority of tetragonal polymorph is needed to retain in the material microstructure. This is due to a very small critical size of the tetragonal grain below which the spontaneous transformation into the monoclinic polymorph does not occur during cooling.[4] Additional factors influencing stability of the tetragonal zirconia polymorph, which are connected with the sintering environment and deoxidation processes, can facilitate the production of the tetragonal zirconia polycrystals by adding CaO (Ca-TZP) with properties as good as those of the Y-TZP or Ce-TZP materials but they has not been recognised in detail yet.

Taking above into consideration, the aim of the presented paper was an attempt to characterise the deoxidation process of the calcia-stabilised TiO_2-added zirconia solid solutions exposed to different sintering environments by means of the X-ray structural analysis.

2. Experiment

Calcium-stabilised TiO_2-added zirconia powders were prepared by means of a co-precipitation method followed by hydrothermal treatment. The molar ratio of CaO to ZrO_2 of 7:93 was kept constant whilst the TiO_2 content changed from 0 to 1.5 mol%. The powders were nano-metric in size (a diame-

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ter of ~8 nm). A detailed description of the powder preparation method can be found elsewhere.[5,6] Four sets of zirconia polycrystals were produced to study response of the zirconia structure to the sintering environment. Two sample sets originated from cold isostatic pressing of the zirconia powders and pressureless sintering of respective green compacts in air (set S/air) or argon (set S/Ar). In the third set (HP/Ar), the zirconia powders were hot-pressed in argon in the unavoidable contact with the graphite foil. The forth set (HP/Ar/WC) differed from the third one in the presence of 10 vol.% WC particulates. The samples were consolidated at the temperatures ranging from 1200 to 1350 °C with a step of 50 °C. Heating rate of 6 °C/min and soaking time of 2 h were used in case of the first two sample sets. The remaining two sets were fabricated using heating rate of 15 °C/min, soaking time of 1 h and pressure of 25 MPa.

Rietveld refinements with X-ray diffraction data were used to determine the phase composition of the sintered bodies and both cell parameters and unit cell volumes of the constituent phases. The samples were polished with diamond powders using 0.25 μm paste in the last polishing step. These were not annealed before X-ray measurements that were performed under the following conditions: anode material—Cu, range—20–120° 2θ, step—0.02° 2θ, counting time—3 s. Refinements were carried out by means of the DBWS-9807a program.[7] The "goodness of fit", S, ranged from 1.91 to 1.99.

The microstructure of the selected samples was observed by means of scanning electron microscopy. A quantitative image analysis performed by using the Aphelion program combined with the Saltykov method[8] were used to determine both median zirconia grain sizes and critical grain sizes of the tetragonal polymorph.

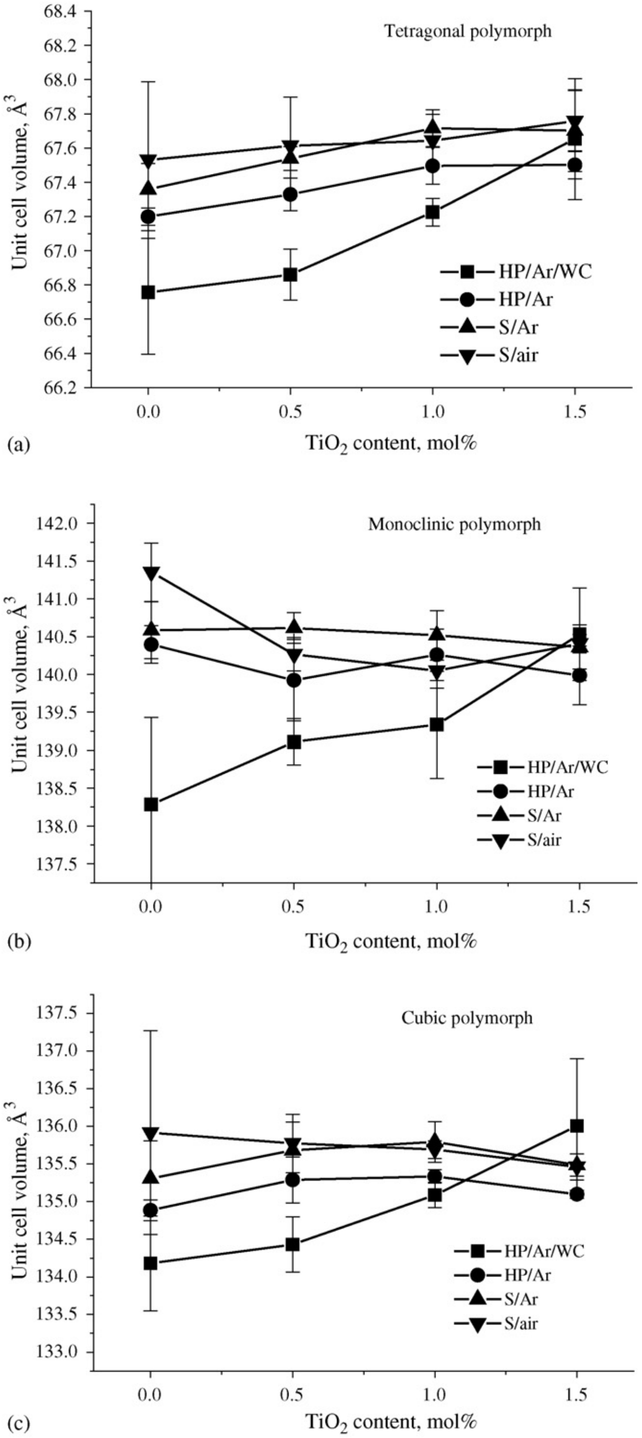

Fig. 1. Unit cell volume vs. TiO$_2$ content for the calcia–zirconia samples sintered at the indicated environments: (a) tetragonal polymorph, (b) monoclinic polymorph, (c) cubic polymorph. Error bars denote standard deviation in the entire work.

3. Results and discussion

The lack of clear-cut dependence of the measured values of cell parameter, axial ratio c/a and unit cell volume of zirconia polymorphs on the sintering temperature was observed for each set of the samples studied. Therefore, average values were calculated within the sintering temperature range applied. For clarity and conciseness of the discussion only the results concerning the unit cell volume and the axial ratio c/a of tetragonal zirconia are presented.

For the calcia-zirconia solid solutions with no TiO$_2$, the unit cell volume of each zirconia polymorph decreased when compared to the samples sintered in air (Fig. 1a–c). This lattice contraction can not be straight related to the increased concentration of oxygen vacancies because each extra vacancy is associated with an increase in the lattice parameter when the zirconia solid solution is exposed to an environment having a low thermodynamic activity.[9,10] The sequence of sintering environments, in which zirconia becomes more and more non-stoichiometric, is as follows: S/air; S/Ar; HP/Ar; HP/Ar/WC. In this sequence, the increased amount of extra oxygen vacancies can be attributed to: (i) smaller oxygen partial pressure in the argon atmosphere (S/Ar samples) than in the air atmosphere (S/air samples), (ii) the presence of carbon from the graphite covers (HP/Ar and HP/Ar/WC samples) which can decrease the oxygen partial pressure in the surrounding atmosphere due to large chemical affinity of carbon to oxygen; the effects of carburisation of the zirconia solid solutions cannot be excluded, (iii) the presence of WC particulates (HP/Ar/WC samples) which increases the concentration of oxygen vacancies due to the beginning of the WC decomposition process induced by oxygen originating from the zirconia

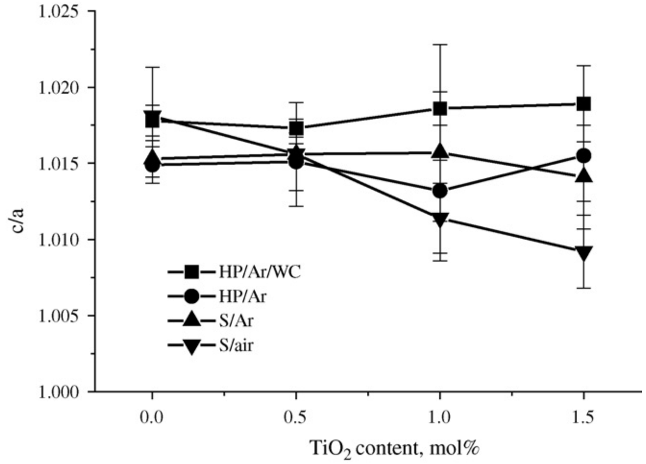

Fig. 2. The axial ratio *c*/*a* of tetragonal zirconia vs. TiO_2 content for the samples sintered at the indicated environments.

solid solution, as suggested by Moskała and Pyda studies.[3] The presented data indicate that factors inducing the lattice contraction predominated the subtle effects of the increased oxygen vacancy concentration. Residual surface stresses seem to be of great importance in this case. They originate from the t → m phase transformation induced at the surface of the materials during polishing. Such surfaces would be expected to be placed in compression[11] giving contribution to the decreased unit cell volumes.

The incorporation of TiO_2 to the calcia–zirconia solid solution tends to inhibit zirconia deoxidation as suggested especially by the decreased unit cell volumes of the cubic zirconia polymorph with the TiO_2 content exceeding 1.0 mol% for the S/air, S/Ar and HP/Ar samples (Fig. 1c). This was also observed in case of the tetragonal and monoclinic zirconia for the S/Ar and HP/Ar samples (Fig. 1a and b). Assuming that TiO_2 has not been reduced within the sintering temperature range and remembering that the $CaO:ZrO_2$ molar ratio was kept constant, the possible mechanism can be attributed to the decreased concentration of the alloying dopant which introduces oxygen vacancies to the system, i.e. calcium oxide. Titanium has smaller ion radius than zirconium and this also contributes to the zirconia lattice contraction. However, the lattice expansion of the zirconia polymorphs is observed in case of the HP/Ar/WC samples. This lattice expansion and any other increase in the zirconia unit cell volume with TiO_2 content can be most probably attributed to the decreased values of compressive residual stresses.

The influence of the sintering environment on the axial ratio *c*/*a* of the tetragonal calcia–zirconia solid solution is shown in Fig. 2. For the zirconia undoped with TiO_2 this influence was insignificant. TiO_2 reduced the axial ratio *c*/*a* of tetragonal zirconia in the oxidizing environment (S/air) and did not change it significantly in the deoxidizing environments (S/Ar, HP/Ar, HP/Ar/WC).

The content of the tetragonal, monoclinic and cubic zirconia in the calcia–zirconia TiO_2-added polycrystals sintered at the applied environments are shown in Fig. 3. Averaging within the sintering temperature range was made also in this case. The large values of standard deviation indicate the expected strong influence of the sintering temperature on phase stability of the calcia–zirconia partially stabilised polycrystals.[4] TiO_2 reduced the tetragonal phase content, increased the monoclinic phase content and practically remained unchanged the content of cubic

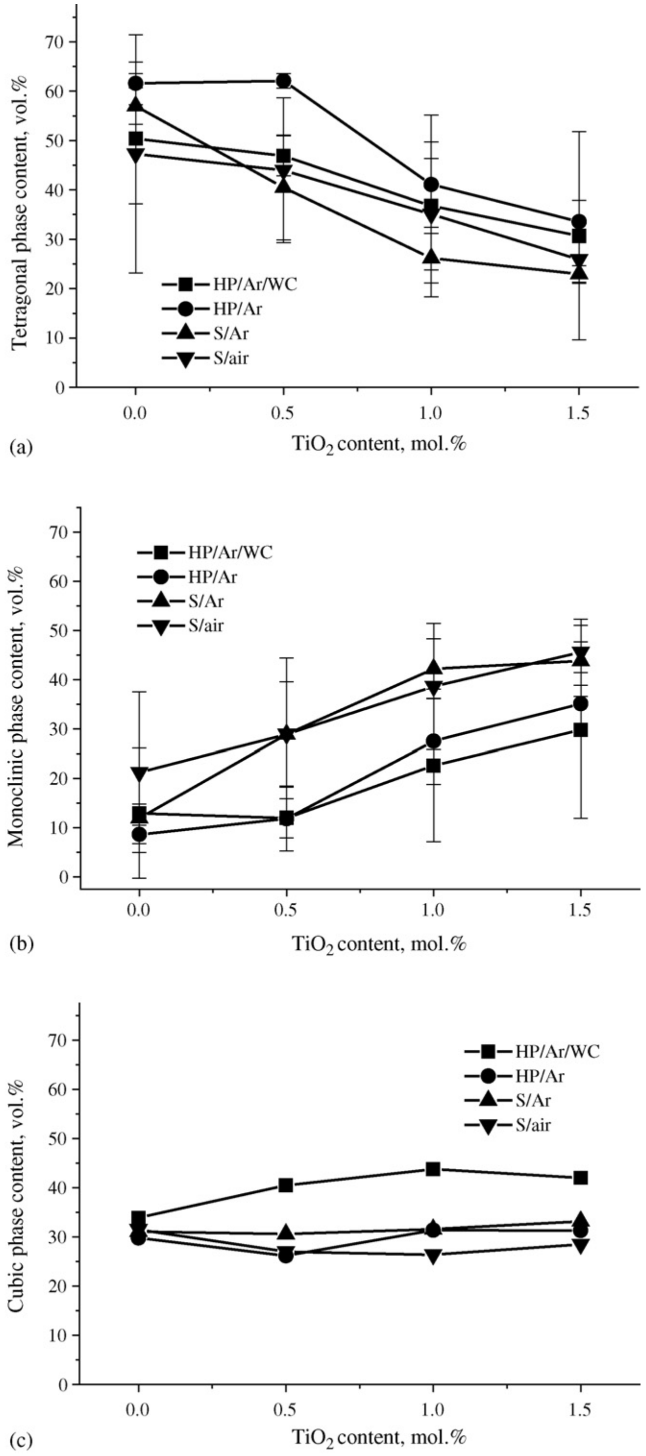

Fig. 3. TiO_2 dependence of zirconia phase content for the samples sintered at indicated environments: (a) tetragonal polymorph, (b) monoclinic polymorph, (c) cubic polymorph. Average values of each zirconia polymorph content within the sintering temperature range of 1200–1350 °C are utilized.

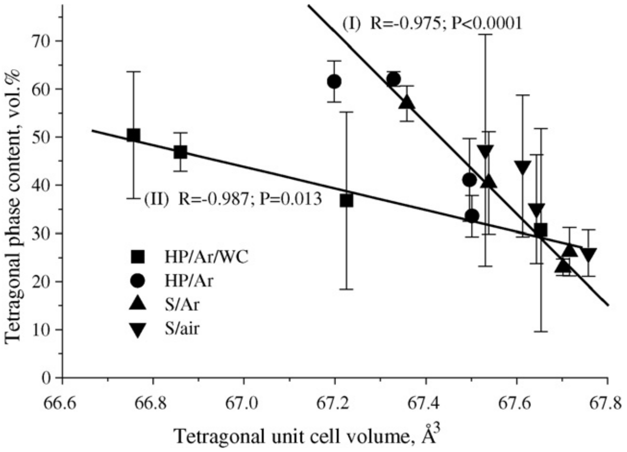

Fig. 4. Content of tetragonal zirconia vs. tetragonal unit cell volume.

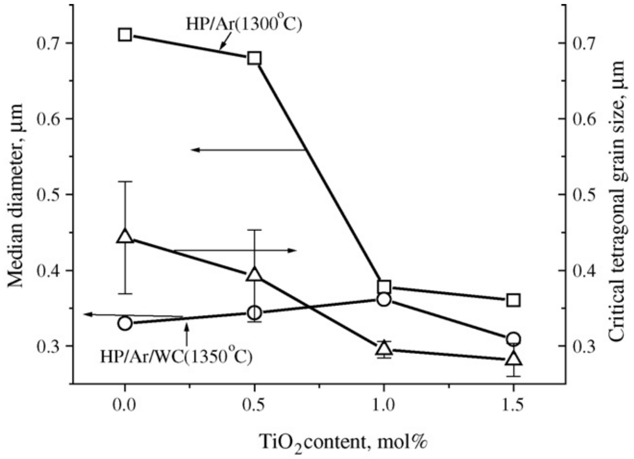

Fig. 5. Median diameter of zirconia grains as a function of TiO_2 content and sintering environment. The HP/Ar and HP/Ar/WC samples sintered at 1300 and 1350 °C were selected, respectively. The figure includes also the TiO_2 dependence of the critical grain size of tetragonal zirconia for 7 mol% CaO–ZrO_2 solid solution.

zirconia. Under such circumstances, some reduction of residual stresses with TiO_2 content is expected as confirmed by the lattice expansion shown in Fig. 1 and by the appearance of cracks in the samples with the largest TiO_2 additions. The content curves of both the monoclinic and tetragonal polymorph are coupled depending on the heating schedule applied: S/air with S/Ar and HP/Ar with HP/Ar/WC. This is a result of the influence of the microstructure (zirconia grain size) on stability of the tetragonal phase. Within each heating schedule the influence of sintering environment on monoclinic phase content was slight suggesting that the microstructure affects stronger stability of the tetragonal phase than the additional oxygen vacancies. The cubic polymorph content was practically insensitive to TiO_2 and sintering environment with the exception of that accompanying the WC presence (HP/Ar/WC).

Combining the data of Figs. 1 and 3 leads to the tetragonal zirconia content–tetragonal unit cell volume diagram shown in Fig. 4. Two linear correlations of high probability level appear in the figure. The data of the HP/Ar, S/Ar and S/air set of samples contribute to the first line (I). The second one (II), is composed of the HP/Ar/WC set of data. The diagram indicates that residual stresses are decisive for the stabilisation of tetragonal zirconia. The larger compressive stresses, which is equivalent to the lower tetragonal cell volume, the larger is the tetragonal phase content. The separation of the additional oxygen vacancy effect from the residual stress effect requires quantitative measurements of both quantities. The presence of two linear correlations suggests that “grain size stabilisation” operates. Microstructural observations of the studied set samples confirmed this suggestion. According to the data shown in Fig. 5, the HP/Ar/WC set of samples contained the polycrystalline materials composed of the zirconia grains smaller or slightly larger than the critical grain size of tetragonal zirconia. On the contrary, the three remaining sets of materials were coarse grained with respect to the critical size of the tetragonal grains. These results show that the tetragonal structure can not be stabilised by doping zirconia crystals with oxygen vacancies only, as is the case of cubic zirconia[1,12] and as it was postulated by Kountouros and Petzow.[13]

4. Conclusions

Deoxidation of the calcia–zirconia solid solutions in the temperature range of 1200–1350 °C due to decreased oxygen partial pressure in the sintering atmosphere does not affect significantly tetragonal phase content appearing to be the weak factor for its probable increase.

Incorporation of TiO_2 to the calcia–zirconia solid solution inhibits zirconia deoxidation due to the dissolution effect, which decreases the oxygen vacancy concentration introduced to the system by alloying with calcium oxide. This leads to decreased amounts of the tetragonal polymorph in the polycrystalline zirconia material.

The reduction of grain size below the critical value is the main stabilising mechanism for the tetragonal zirconia polymorph in the partially stabilised zirconia polycrystals. The additional oxygen vacancy mechanism requires further experimental evidences.

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