

Influence of Ca^{2+} and Mg^{2+} as twinned ions on zirconia powder stability

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Microstructure and the sintering behaviour of zirconia with twinned stabiliser ions: $\text{Ca}^{2+} + \text{Mg}^{2+}$ in oxidative and in inert environment respectively obtained by solid state reactions method were studied. The specimens were cured at 1550 °C and 1750 °C in air in a kiln with methane gas. Samples with the same composition were sintered at 1550 °C in Argon in electrical furnace with (graphite electrodes). Their sinterability, microstructure as well as stability was studied. The properties were compared as function of the processing route, the compositions stabilised in argon protective environment at 1550 °C or in air at 1750 °C, a totally stabilisation process was effective.

(Received January 18, 2006; accepted March 23, 2006)

Keywords: Zirconia, Stabilisation, Sintering

1. Introduction

The stabilisation of zirconia products are now intensively studied domains as a result of their good mechanical and corrosion resistance at high temperatures [1-3]. This process leads to the fully or partially stabilisation of zirconia and may be achieved by inserting in ZrO_2 lattice some ions having similar ion radius comparatively to that of Zr^{4+} . In such way the tetragonal (t) or cubic (c) polymorph become stable at room temperature [4].

Stabilisation in binary systems is a very widely approached process, but in many cases the temperatures needed for its achievement are too high and sometimes, even if tetragonal solid solutions are formed, they are unstable and are changing into a monoclinic structure on cooling. Due to these reasons, the modern researches regarding the stabilisation process are focused towards ternary systems [5-10]. The high fracture toughness of optimally processed precipitation toughened partially stabilised ZrO_2 's (PSZ's) is due to the stress induced martensitic transformation of tetragonal (t) precipitates to monoclinic (m) form in the stress fields of propagation crack. PSZ's are two phase ZrO_2 alloys, the matrix phase is a solute rich cubic (c)- ZrO_2 solid solution, which contains fine tetragonal (t)- ZrO_2 precipitates of a lower solute content. Consequently, this paper aims the study of stabilisation in argon environment comparatively with oxidising temperature at 1550 °C of some ternary composition belonging to the ZrO_2 -CaO-MgO system.

2. Experimentals

As starting materials were used unstabilised zirconia (Toshok) with 99.5% $\text{ZrO}_2 + \text{HfO}_2$, density of 4.763 g/cm³

having an average grain size, $d_{\text{avg}} = 0.9 \mu\text{m}$. As stabilising oxides were used CaO and MgO starting from CaCO_3 (Reactivul Bucuresti grade), (99.9% CaCO_3 , $d_{\text{avg}} = 22.7 \mu\text{m}$) and dead burned MgO (Ocna-Mures grade (99.8% MgO, $d_{\text{avg}} = 8.6 \mu\text{m}$).

Zirconia and stabilising oxides mixtures batches were prepared according to Table 1, starting from 88-96 % (wt%) monoclinic zirconia powder and 2 - 11 % CaO (by weight). MgO as secondary stabilising oxide (1 - 10 wt %) was added in an attritor with isopropanol using zirconia balls, for 2 hours.

Table 1. The composition of monoclinic ZrO_2 and stabilising oxides mixture in ZrO_2 -CaO-MgO system.

Specimens	ZrO_2 (wt %)	CaO, (wt %)	MgO, (wt %)
A1	96	3	1
A2	94	4	1
A3	92	7	10
A4	90	9	1
A5	88	11	1
A6	94	4	2
A7	94	3	3
A8	94	2	4

After drying the powder mixtures were passed through a 0.5 mm sieve. The batches were pressed as cylinders ($\phi = h = 18 \text{ mm}$). The specimens were cured at 1550 °C and 1750 °C in air in a kiln with methane gas, during 8 hours. Samples with the same composition were sintered at 1550 °C in Argon in electrical furnace with (graphite electrodes) for 2 hour at maximum temperature.

A TUR - 4 diffractometer with Cu K_{α} radiation was used to analyse the developed mineralogical phases. The particles size distribution of the powders was determined by using a laser granulometer (Fritsch). The sintering bulk density was measured by the hydrostatic method.

A Hitachi S 2600N scanning electron microscope (SEM) incorporating a microanalysis detector for energy dispersive X-rays (EDS) was used to observe the surface microstructure of samples .

3. Results and discussion

3.1. Ceramic properties

In Fig. 1 are presented the ceramic properties of zirconia samples (A1 –A8) belonging to ZrO_2 -CaO-MgO system after sintering at 1550 °C and 1750 °C in air and at 1550 °C in argon and the same behaviour of the samples is registered like in ZrO_2 -CaO-MgO system.

3.2. Microstructure

XRD patterns of A1, A6, A7 and A8 ternary zirconia powders stabilised in Argon atmosphere are given in Fig. 2 and in oxidising atmosphere at 1550 °C are shown in Fig. 3.

XRD patterns of the same samples stabilised in oxidising atmosphere at 1750 °C are shown in Fig. 4. The X-ray diffraction analysis on the samples A1, A6, A7, A8 fired in argon at 1550 °C (Fig. 2) emphasised totally stabilisation process of zirconia when cubic and tetragonal solid solutions are present. The firing of the samples A1 and A8 in air at 1550 °C (Fig. 3) leads to the developing of partially stabilised zirconia consisting of cubic solid solutions as major phase, tetragonal phase in low amount and monoclinic polymorph, and the compositions A6 and A7 are totally stabilised. After firing at 1750 °C in air (Fig. 4), only the cubic zirconia was detected on all samples.

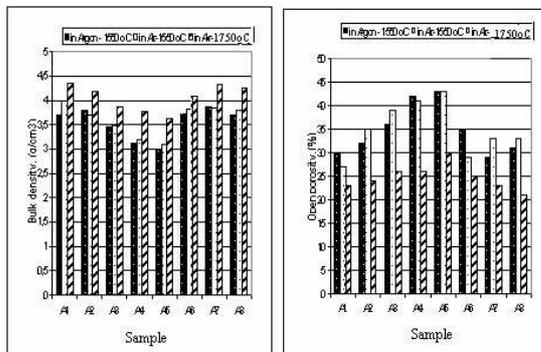


Fig. 1. The ceramic properties of ZrO_2 -CaO-MgO powders after sintering at 1550 °C and 1750 °C in air and at 1550 °C in argon respectively.

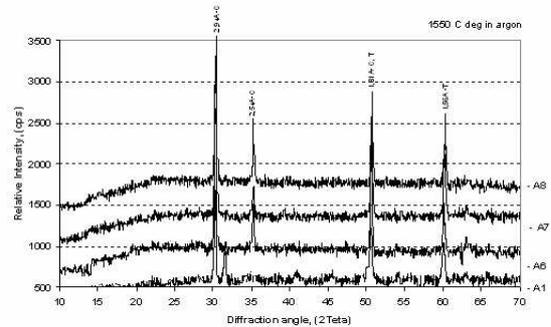


Fig. 2. XRD patterns of A1, A6, A7 and A8 compositions in ZrO_2 -CaO-MgO system fired in Argon at 1550 °C (where: C-cubic $ZrO_{2(ss)}$, T-tetragonal $ZrO_{2(ss)}$).

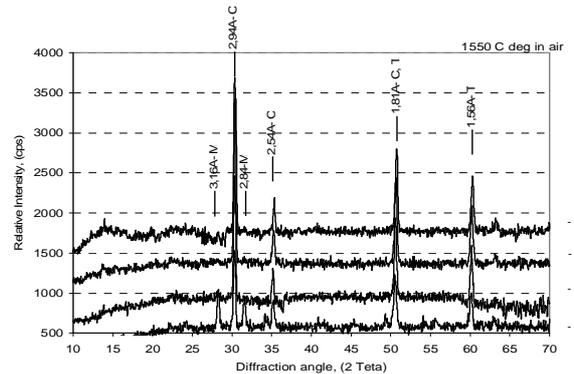


Fig. 3. XRD patterns of A1, A6, A7 and A8 compositions in ZrO_2 -CaO-MgO system fired in air at 1550 °C (where: M-monoclinic $ZrO_{2(ss)}$, T- tetragonal $ZrO_{2(ss)}$, C-cubic $ZrO_{2(ss)}$).

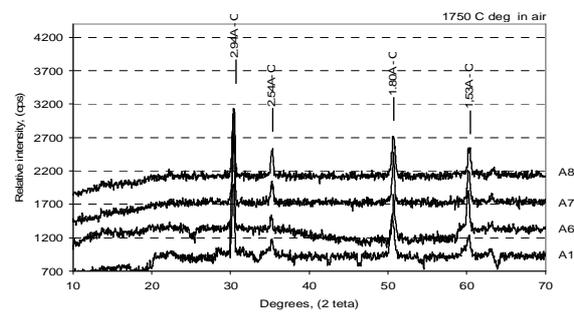
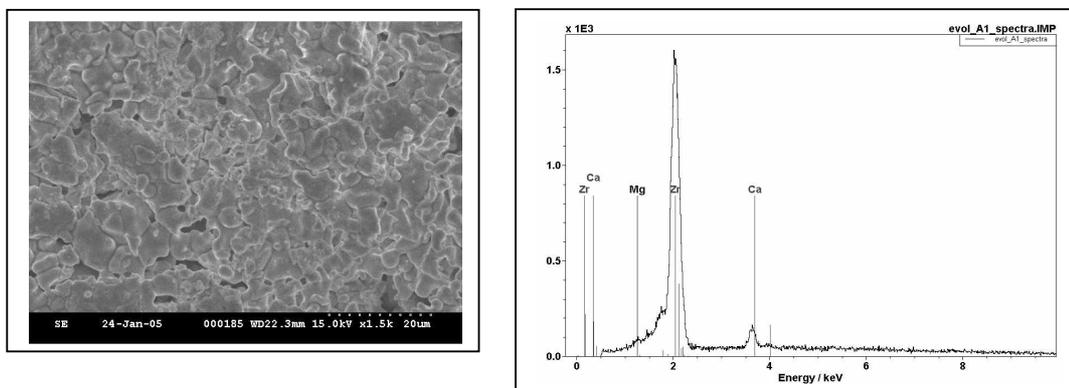


Fig. 4. XRD patterns of A1, A6, A7 and A8 compositions in ZrO_2 -CaO-MgO system fired in air at 1750 °C (where: C - cubic $ZrO_{2(ss)}$).

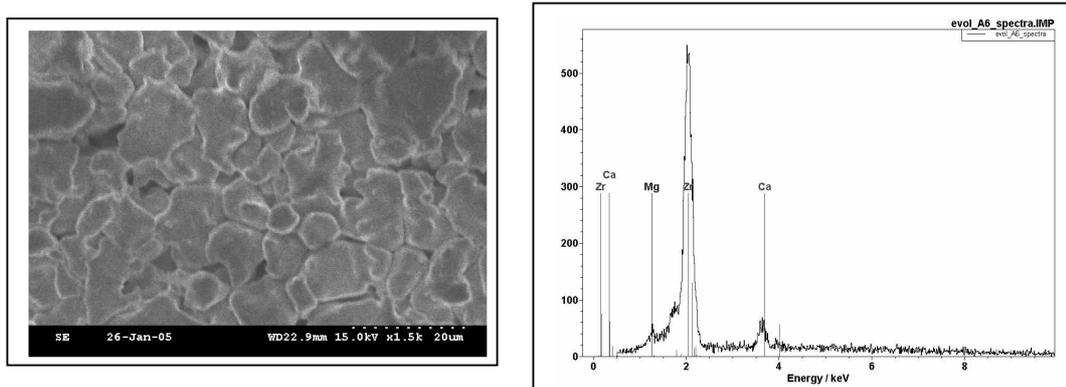
SEM micrographs and EDS signals from the samples A1, A6, A7 and A8 fired in Argon at 1550 °C are shown in Figs. 5-8. The stabilising element Mg and Ca are revealed on samples surface.



(a)

(b)

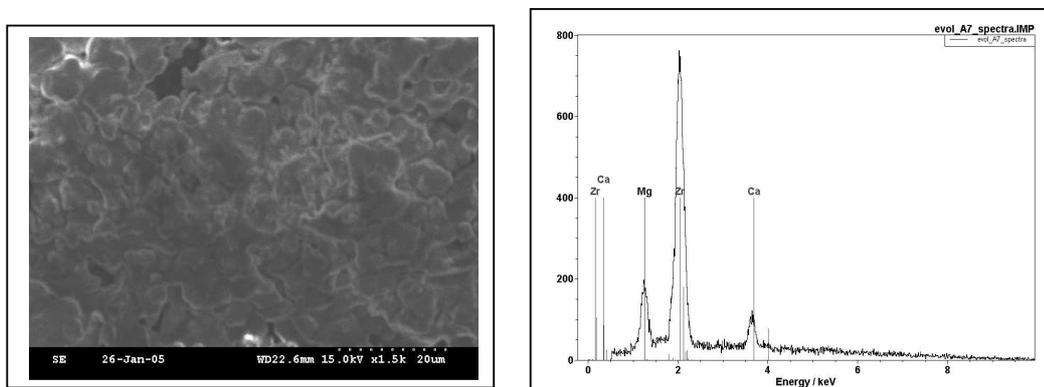
Fig. 5. SEM micrograph (a) and EDS signals on A1 (3% CaO + 1%MgO) sample surface (b) fired at 1550 °C in argon.



(a)

(b)

Fig. 6. SEM micrograph (a) and EDS signals on A6 (4% CaO + 2%MgO) sample surface (b) fired at 1550 °C in argon.



(a)

(b)

Fig. 7. SEM micrograph (a) and EDS signals on A7 (3% CaO + 3%MgO) sample surface (b) fired at 1550 °C in argon.

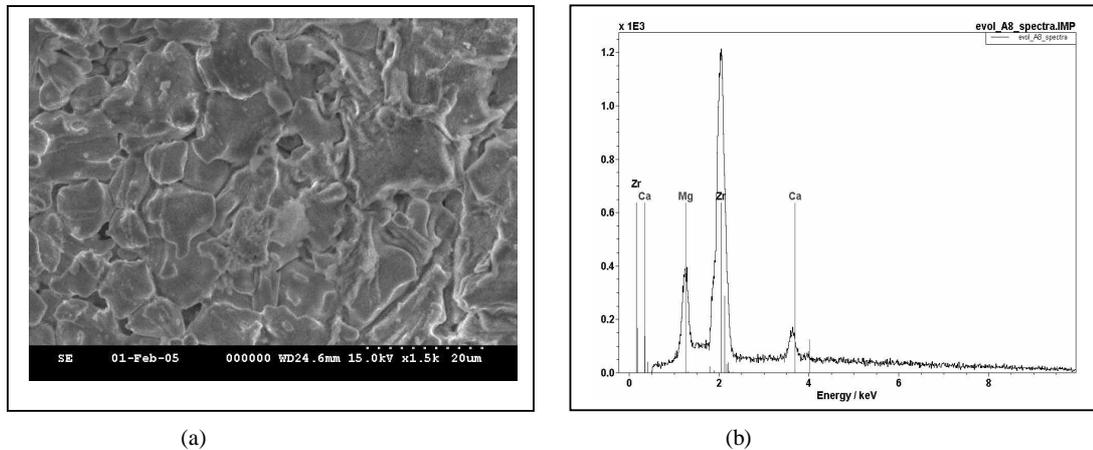


Fig. 8. SEM micrograph (a) and EDS signals on A8 (2% CaO + 4% MgO) sample surface (b) fired at 1550 °C in argon.

4. Conclusions

The results highlighted the possibility of fully or partially stabilisation of some compositions belonging to ZrO_2 –CaO–MgO system, cured in air and in argon.

The sintering conditions (in air or in argon) seem to have a great influence and determine major changes on ratio between zirconia polymorphs. Argon protective environment at 1550 °C induces the decreases of the amount cubic and tetragonal polymorphs of zirconia, while the oxidising curing at the same temperature leads to the decreases of monoclinic polymorph.

For the compositions stabilised in argon protective environment at 1550 °C or in air at 1750 °C a totally stabilisation process was effective.

Acknowledgement

Part of this work has been performed in the framework Romanian National R&D Programme, CERES Project, (No. 4 -78/ 2004).

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