

Microstructure and Thermal Stability of Fine-grained (Y, Mg)-PSZ Ceramics with Alumina Additions

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(Received 13 July 1992; revised version received 12 October 1992; accepted 3 November 1992)

Abstract

Commercial powders within the system ZrO_2 – MgO – Y_2O_3 – Al_2O_3 were used to produce zirconia ceramics with improved thermal stability. Different sintering routes were followed in order to determine the optimum conditions. Fine-grained (Y, Mg)-PSZ ceramics with grain sizes below $10\ \mu m$ were achieved. Microstructural evolution was studied after various isothermal heat treatments. After ageing, the materials contain a large fraction of tetragonal phase which does not transform after a hydrothermal ageing treatment in an autoclave, but can still be transformed under mechanical stress.

Kommerzielle Pulver aus dem System ZrO_2 – MgO – Y_2O_3 – Al_2O_3 wurden zur Herstellung von ZrO_2 -Keramiken mit verbesserter thermischer Stabilität verwendet. Mit Hilfe unterschiedlicher Sinterzyklen wurden die Herstellungsbedingungen optimiert. Feinkörnige (Y, Mg)-PSZ-Keramiken mit Korngrößen $< 10\ \mu m$ wurden erzielt. Die Gefügeentwicklung wurde in Abhängigkeit unterschiedlicher isothermer Alterungsbehandlungen untersucht. Nach einer optimierten Alterung enthalten die Proben einen hohen Anteil tetragonaler Phasen, die zwar spannungs-induziert umwandelbar sind, aber unter hydrothermalen Bedingungen im Autoklaven nicht in die monokline Form umwandeln.

Des poudres commerciales appartenant au système ZrO_2 – MgO – Y_2O_3 – Al_2O_3 ont été utilisées pour produire des céramiques en zirconie avec une stabilité thermique accrue. Différentes méthodes de frittage ont été suivies dans le but de déterminer les conditions

optimales. Des céramiques (Y-Mg)-PSZ à fins grains avec des tailles de particules sous $10\ \mu m$ ont été réalisées. L'évolution microstructurale a été étudiée après différents traitements en isotherme. Après vieillissement, les matériaux contiennent une grande fraction de phase quadratique qui ne se transforme pas après un traitement hydrothermal en autoclave, mais peut toujours être transformée sous l'effet de contraintes mécaniques.

1 Introduction

Yttria-doped tetragonal zirconia polycrystals (Y-TZP) exhibit very high strength and toughness.^{1–3} However, these ceramics degrade at low temperatures ($\approx 200^\circ C$), especially when exposed to a humid atmosphere. The reaction of water with the small ($< 1\ \mu m$) tetragonal grains of Y-TZP materials leads to an uncontrolled tetragonal (t) to monoclinic (m) phase transformation. Due to the associated volume expansion, microcracking occurs, which proceeds from the surface into the bulk. As a result of this process, strength decreases dramatically.^{4–6}

Mg-partially stabilized zirconia (Mg-PSZ) exhibits much better resistance to low-temperature ageing, although some strength degradation was also observed in some cases.^{7,8} The strength of Mg-PSZ is lower than that of Y-TZP, but its fracture toughness is much higher.^{9–12}

The ternary system ZrO_2 – MgO – Y_2O_3 has mainly been studied with respect to the effect of yttria on the subeutectoid decomposition of Mg-PSZ. During ageing at temperatures between $1000^\circ C$ and $1400^\circ C$, the cubic (c) phase decomposes either into t- ZrO_2 and MgO or into m- ZrO_2 and MgO, respectively,

Table 1. Compositions of the powder mixtures used

Sample designation	Matrix composition (mol%)			Additions (vol.%)	
	Y ₂ O ₃	MgO	ZrO ₂	Al ₂ O ₃	MgO-Al ₂ O ₃
A-3A	1.5	5.0	93.5	3.0	—
A-3S	1.5	5.0	93.5	—	3.0
B	0.8	7.1	92.1	—	—
B-3A	0.8	7.1	92.1	3.0	—
B-3S	0.8	7.1	92.1	—	3.0

leading to strength degradation. Thus the maximum long-term application temperature of Y₂O₃-free Mg-PSZ is limited to $\approx 900^\circ\text{C}$.¹¹ Addition of Y₂O₃ effectively suppresses this decomposition up to 1250°C .^{13,14}

In a more recent study on the precipitation behaviour in (MgO, Y₂O₃)-ZrO₂ it has been found that the transformable tetragonal phase is difficult to precipitate.¹⁵ A maximum volume fraction of 12% of transformable phase was found after isothermal heat treatment up to 5000 h at temperatures between 1000°C and 1400°C . Consequently, stress-induced transformation plays a lesser role as a toughening mechanism than microcracking.

The aim of this work was to produce a fine-grained Mg-PSZ-type material with better low-temperature stability than Y-TZP and good mechanical properties.¹² For this purpose, Al₂O₃ was added to compositions from the ZrO₂-MgO-Y₂O₃ system.

2 Experimental Procedures

Mixtures of the five compositions listed in Table 1 were prepared from commercial powders of 3 mol% Y₂O₃-containing ZrO₂ (TZ3Y, Tosoh Co. Ltd, Tokyo, Japan) and 9 mol% MgO-ZrO₂ (SCMG3 Grade, Magnesium Elektron Ltd, Manchester, UK) as well as pure Al₂O₃ (Alcoa A-16, Alcoa, Pittsburg, USA) and MgO (Merck, Darmstadt, Germany) as additives. The materials are basically composed of Y₂O₃- and MgO-containing ZrO₂ powders. Two ratios were selected, resulting in compositions of 1.5 mol% Y₂O₃-5.0 mol% MgO-93.5 mol% ZrO₂ and 0.8 mol% Y₂O₃-7.1 mol% MgO-92.1 mol% ZrO₂, denoted A and B, respectively. To each of these compositions 3 vol.% of Al₂O₃ or

3 vol.% of a separately prepared mixture of Al₂O₃ and MgO was added, referred to below as A-3A, B-3A, A-3S and B-3S. The Al₂O₃/MgO mixture had a 1:1 ratio, suitable for the formation of MgAl₂O₄ spinel.

The mixtures were wet milled in ethanol with 3Y-TZP milling media in polyethylene bottles. After a milling time of 24 h the powders were dried. Green bodies were formed by uniaxial pressing in a steel die at 35 MPa followed by cold isostatic pressing at 150 MPa. The discs obtained measured about 28 mm in diameter and 5 mm in thickness.

The discs were sintered in air at temperatures between 1400°C and 1700°C with different holding times. The typical processing parameters are reported in Table 2. 3Y-TZP were used as sintering supports in the furnace. Samples sintered at 1700°C for 1 h were subsequently aged at 1400°C for a period ranging from 1 to 10 h. The optimum ageing condition was determined by X-ray analysis comparing the (202) and (220) peak intensities. CuK _{α} radiation was used. The monoclinic phase contents were evaluated using the method proposed by Garvie & Nicholson.¹⁶

Densities of the sintered samples were measured by Archimedes' method and the relative densities were calculated, taking the c-, t- and m-ZrO₂ and spinel volume content into account.

Microstructures of thermally etched samples were examined by scanning electron microscopy. Grain sizes were estimated by the line intercept method.

In order to study the hydrothermal stability, the samples were treated in an autoclave with water vapour at 180°C and a pressure of 10 bar for up to 40 h. The transformable t-phase content present after the hydrothermal ageing treatment was examined by surface grinding and measuring the m-phase content.

Table 2. Sintering conditions and final densities (g/cm³) after different sintering cycles

Material	1400°C, 10 h	1500°C, 3 h	1600°C, 3 h	1700°C, 1 h
A-3A	5.51	5.65	5.65	5.64
A-3S	5.41	5.59	5.66	5.69
B	5.39	5.43	5.58	5.64
B-3A	5.38	5.59	5.65	5.64
B-3S	5.38	5.47	5.63	5.67

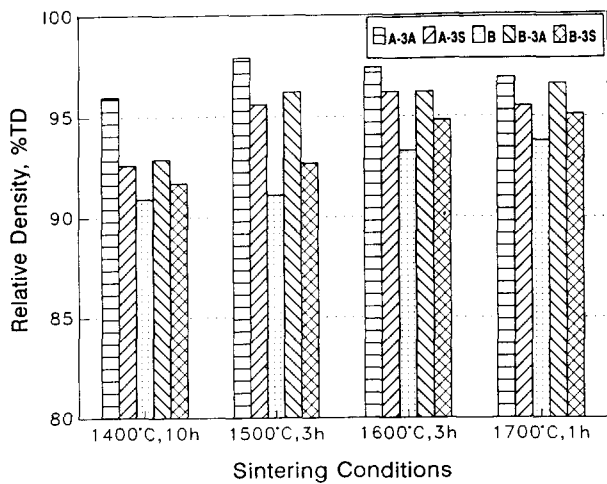


Fig. 1. Comparison of relative densities obtained after different sintering conditions.

3 Results and Discussion

3.1 Sintering

Dense samples with a residual porosity between 3% and 10% are obtained after sintering at 1400°C for 10 h, 1500°C for 3 h, 1600°C for 3 h and 1700°C for 1 h. The relative densities are given in Fig. 1. Under all sintering conditions, samples A-3A and B-3A, both containing Al_2O_3 additions, show relative densities higher than that of samples A-3S and B-3S with additions of the Al_2O_3 -MgO mixture.

Material B, prepared without additions, exhibits consistently the lowest relative density. Comparing the relative densities of samples B, B-3A and B-3S it becomes obvious that both Al_2O_3 and MgO- Al_2O_3 additions aid in the sintering of the matrix.

It is assumed that the improved densification behaviour of the Al_2O_3 -containing samples is due to a liquid-phase sintering process as observed in TEM examinations by Rühle *et al.*¹⁷ of Al_2O_3 -containing Y-TZP. However, no TEM examinations had been performed so far on these materials to verify this hypothesis.

X-Ray analysis reveals that all sintered samples, with the exception of material B, contain a small amount of MgAl_2O_4 spinel. Pure alumina is not detectable. Furthermore, samples A-3A and B-3A exhibit very high m-phase contents, as shown in Fig. 2, ranging from 46 to 68 vol.% for sample A-3A and from 31 to 56 vol.% for sample B-3A. The m-phase contents of samples with MgO- Al_2O_3 additions range only from 13 to 41 vol.% for sample A-3S, and from 4 to 32 vol.% for sample B-3S. These results indicate that the Al_2O_3 powder present in samples A-3A and B-3A reacts with the matrix MgO to form MgAl_2O_4 spinel. As a consequence the matrix is destabilized, and a large amount of m-phase is formed during cooling. In samples A-3S and B-3S, the spinel particles are formed from the added

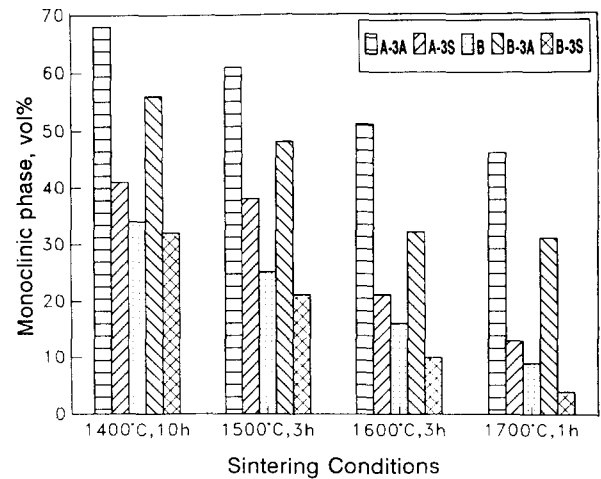


Fig. 2. Comparison of monoclinic phase content obtained after different sintering conditions.

MgO- Al_2O_3 mixtures. Hence the MgO content in the 9% MgO- ZrO_2 powder is not consumed.

Considering the cubic and tetragonal peak intensities, it can be concluded that sintering at 1700°C for 1 h leads to the highest amount of t- and the lowest content of m-phase. For this reason, attention was focused on samples sintered at 1700°C for 1 h.

3.2 Isothermal ageing

Ageing of samples A-3S and B-3S at 1400°C, performed in order to coarsen the t-precipitates, leads to an increase in the t-phase content. The diffraction pattern of sample B-3S in Fig. 3 shows the evolution of the t-phase (202) and (113) peaks during ageing. Note the increased t-phase (202) and (113) peak intensities after 1 h ageing. Ageing for 10 h results in the formation of m-phase and in a reduction of the t-phase content. From the calculated intensity ratios of the t-phase (202) and the c-phase (220) peaks presented in Fig. 4, it is concluded that the optimum ageing time is 1 h for material B-3S and 3 h for material A-3S.

The reduction of the t-phase content after 10 h of ageing and the increase in the m-phase content indicate an overageing, well known from Mg- and Ca-PSZ materials.^{10,18} In these materials, excessive ageing times lead to a coarsening of the precipitates above the critical size for spontaneous transformation. Hence, the m-phase content increases. The increase in m-phase content in samples A-3A, A-3S, B-3A and B-3S with increasing ageing time is shown in Fig. 5. From this diagram it can be further seen that, in sample B-3S, the t-phase transforms more readily during ageing when compared to material A-3S. The reason may be the lower content of yttria as well as larger t-precipitates, close to the critical size.

It should be noted that, after ageing at 1400°C for 10 h, no MgO was detected by X-ray analysis. So the

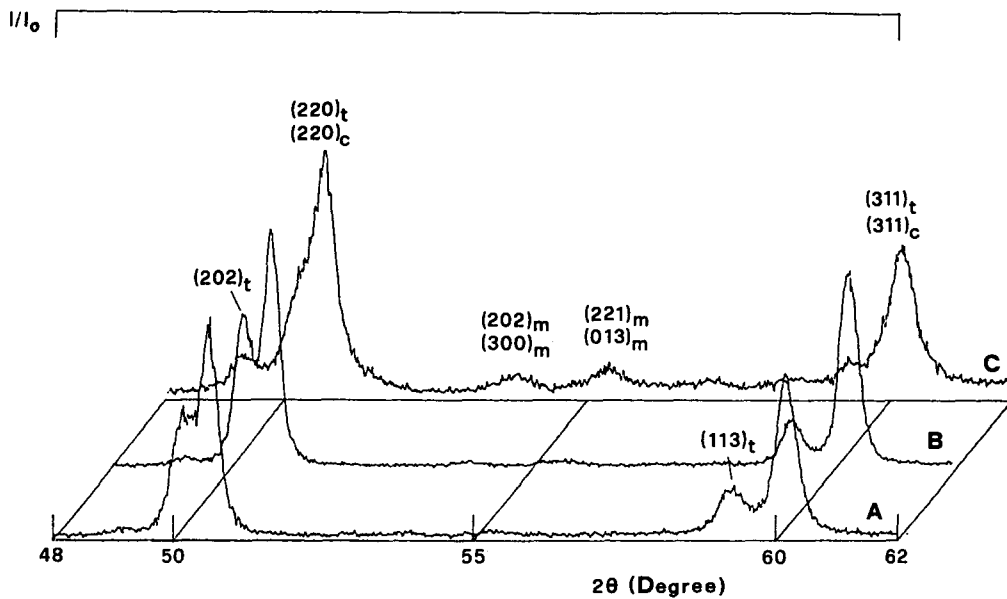


Fig. 3. Diffraction pattern scans of material B-3S. (A) As-sintered (1700°C for 1 h), (B) after additional heat treatments at 1400°C for 1 h, and (C) after 10 h of ageing.

materials seem to be stable against eutectoid decomposition at this temperature, and the increase in m-phase is related only to overageing.

Photographs of the characteristic microstructure common to the materials are shown in Figs 6 to 9. All samples exhibit a bimodal grain size distribution of small m-grains, identified by the twinned structure, and large c-grains. This bimodal distribution is very pronounced in material B (see Fig. 6).

The quantity of twinned m-grains is highest in material A-3A, a result which is consistent with X-ray analysis. The mean size of the m-grains in material A-3A is approximately 2 µm, whereas the mean size of the c-grains is approximately 4 µm.

Materials A-3S, B, B-3A and B-3S show the same size of m-grains, but there is a significant difference in the c-grain size. In contrast to material A-3A, material A-3S showed an increased c-grain size of approximately 6 µm. This suggests that the grain size is sensitively controlled by the amount of

Al₂O₃ additions which act in limiting grain growth. The grain boundary pinning of MgAl₂O₄ spinel particles is visualized by dark contrast in Fig. 7 for sample A-3A.

The same grain-growth hindering mechanism of the Al₂O₃ additions was observed in materials B, B-3S and B-3A. Materials B, without any additions, has a mean c-grain size of 7.0 µm, with additions of 3 vol.% of MgO–Al₂O₃ a mean c-grain size is 6.5 µm and with additions of 3 vol.% of Al₂O₃ it is only 4.5 µm. This c-grain size is small when compared to that of commercial 9% Mg-PSZ materials.

Analysing samples A-3A and A-3S with SEM, the lenticular-shaped tetragonal precipitates within cubic grains, as known from pure Mg-PSZ materials, could not be observed. On the contrary, in all three B materials with the matrix composition of 0.8 mol% Y₂O₃–7.1 mol% MgO–92.1 mol% ZrO₂ the formation of precipitates can clearly be seen. The precipitates in sample B-3S show two different structures. In addition to the elongated, lenticular-

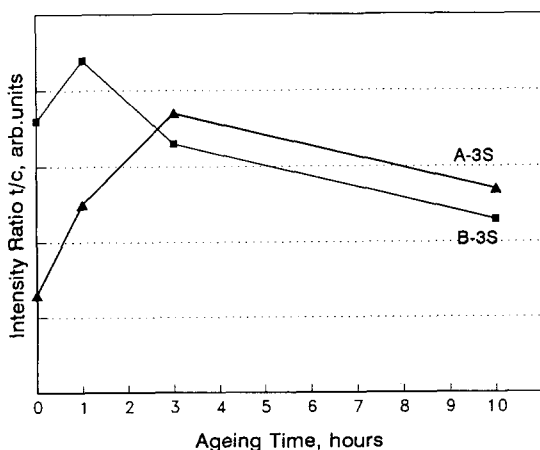


Fig. 4. Tetragonal phase content versus ageing time at 1400°C. The maximum for material B-3S is achieved after 1 h, and for material A-3S after 3 h of ageing.

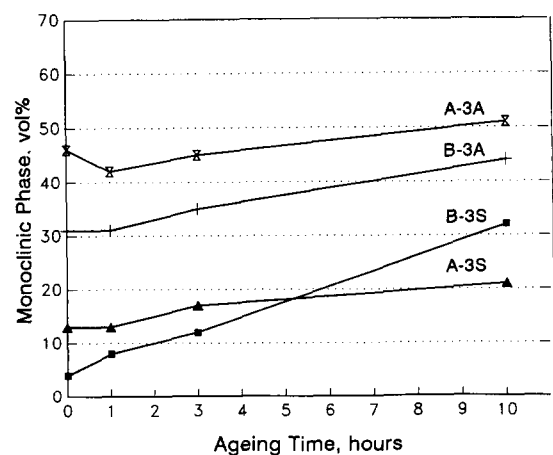


Fig. 5. Monoclinic phase content versus ageing time at 1400°C.

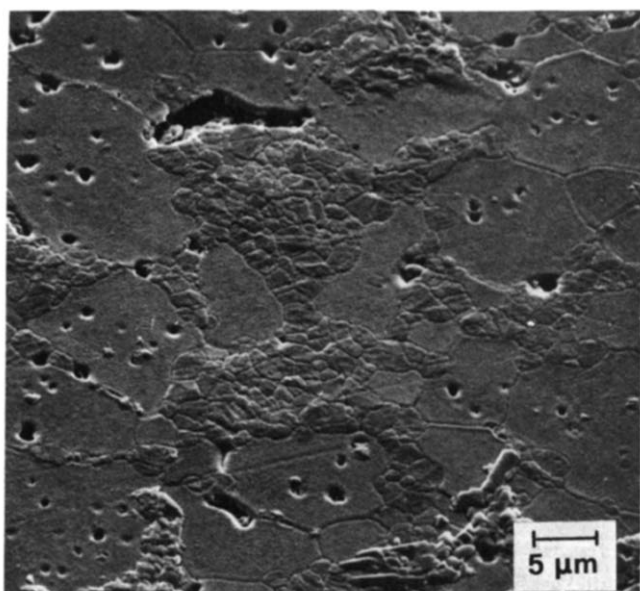


Fig. 6. Scanning electron micrograph of material B after sintering at 1700 °C for 1 h and subsequent ageing at 1400 °C for 3 h. Cubic grains grow large without alumina additions.

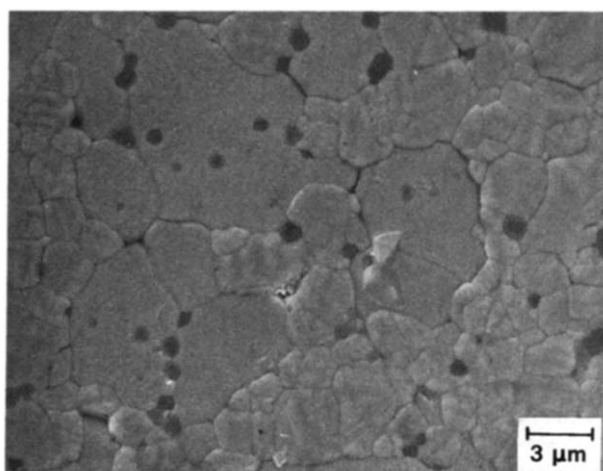


Fig. 7. Scanning electron micrograph of material A-3A sintered at 1700 °C for 1 h and subsequently aged at 1400 °C for 3 h.

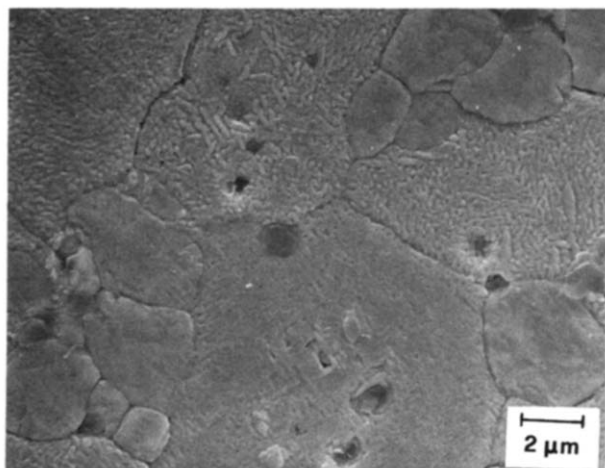


Fig. 8. Scanning electron micrograph of material B-3S after sintering at 1700 °C for 1 h and subsequent ageing at 1400 °C for 3 h. Note the tetragonal precipitate in cubic grains.

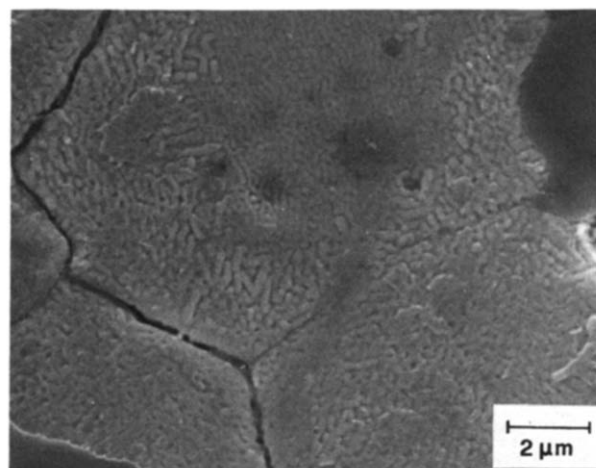


Fig. 9. Brain-like structure of tetragonal precipitates within cubic grains of material B-3S sintered at 1700 °C for 1 h and aged at 1400 °C for 3 h.

shaped precipitates, there are regions within cubic grains with a more irregular, brain-like structure (Figs 8 and 9). This irregular structure inside the c-grains was previously observed by Yuan *et al.*¹⁹ in dual-phase MgO–ZrO₂ ceramics and are thought to be domains of the tetragonal t'-phase.

3.3 Hydrothermal ageing treatment

As only materials A-3S and B-3S, sintered at 1700 °C for 1 h and aged at 1400 °C for 3 h, exhibited a low m-phase and a high t-phase content, these samples were used to examine thermal stability under hydrothermal conditions.

After exposure for 40 h, sample A-3S shows no increase in m-phase content, as indicated in Fig. 10. Thus the thermal stability is very good when compared with pure 3Y-TZP. The values for 3Y-TZP were taken from Hirano & Inada.²⁰ Similarly, good thermal stability is observed for the sample B-3S. After hydrothermal treatment for 20 h, the m-phase content increased from 12 vol.% in the

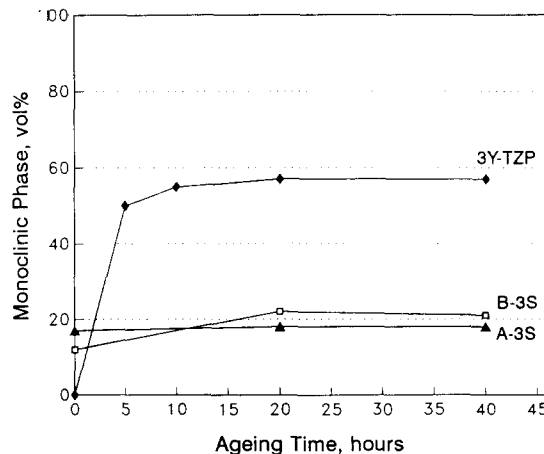


Fig. 10. Monoclinic phase content after hydrothermal ageing of samples A-3S and B-3S in an autoclave with water vapour at 180 °C and 10 bars. Values for 3Y-TZP after Hirano & Inada.²

starting material to 22 vol.%. Extended ageing to 40 h does not further increase the m-phase content.

In order to verify whether the tetragonal precipitates are still able to transform into m-phase after the hydrothermal treatment, the samples exposed for 40 h were ground and subjected to X-ray analysis. The A-3S material shows an increment of about 11 vol.% in m-phase up to the value of 29 vol.% after grinding. In spite of the slightly higher m-phase content, material B-3S appears to be more susceptible to stress-induced transformation as the grinding procedure increases the m-phase content from 22 vol.% to 49 vol.%.

4 Conclusions

Starting from commercial 3 mol% Y_2O_3 - and 9 mol% MgO-containing powders, ZrO_2 materials with a fine-grained microstructure similar to Mg-PSZ with cubic grain sizes $< 10 \mu m$ can be produced if small amounts of Al_2O_3 and MgO- Al_2O_3 are added.

Both Al_2O_3 as well as MgO- Al_2O_3 additions promote sintering, as verified for one type of (Y, Mg)-PSZ material, and reduce grain growth.

With appropriate ageing treatment high amounts of tetragonal phase can be precipitated.

After hydrothermal treatment up to 40 h the materials exhibit much better thermal stability than conventional Y-TZP. Nevertheless, a large amount of tetragonal phase is still able to transform into monoclinic symmetry under mechanical stress. This behaviour is very promising in terms of toughening.

Acknowledgements

The authors are grateful to CEC for providing F. Meschke with a grant from the Brite/Euram program (contract number Breu-900298). The supply of ZrO_2 powders (SCMG3) by Magnesium Electron Ltd, Manchester, UK is gratefully acknowledged.

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