

Sintering behaviour and microstructure of 3Y-TZP + 8 mol% CuO nano-powder composite

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Abstract

Nanocrystalline 3Y-TZP and copper-oxide powders were prepared by co-precipitation of metal chlorides and copper oxalate complexation-precipitation, respectively. A significant enhancement in sintering activity of 3Y-TZP nano-powders, without presence of liquid phase, was achieved by addition of 8 mol% CuO nano-powder, resulting in an extremely fast densification between 750 and 900 °C. This enhancement in sintering activity was explained by an increase in grain-boundary mobility as caused by dissolution of CuO in the 3Y-TZP matrix. The nano-powder composite was densified to 96% by pressureless sintering at 1130 °C for 1 h. Considerable tetragonal to monoclinic phase transformation of the zirconia phase was observed by high temperature XRD analysis. This zirconia phase transformation is discussed in terms of reactions between CuO and yttria as segregated to the 3Y-TZP grain boundaries.

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1. Introduction

Zirconia based ceramic materials have obtained extensive interest in the past decades due to their advanced mechanical and electrical properties. The high fracture toughness and strength of 3 mol% yttria stabilised tetragonal zirconia polycrystals (3Y-TZP) make this material an important candidate for many structural applications.^{1,2} Yttria doped cubic zirconia ceramics showing high ionic conductivity and are widely used as electrolytes in fuel cells and oxygen sensors.^{3,4} It was also reported that fine-grained Y-TZP ceramics exhibit a superplastic deformation property, which has opened up the possibility of using ceramics in ductile near net shape forming operations.⁵ Recently low dry sliding friction was obtained with CuO doped 3Y-TZP ceramics,^{6,7} implying a possibility of engineering applications of these materials without lubricants.

Many efforts have been addressed on enhancing the sinterability of zirconia-based ceramics because it is important not only for production cost, but also for development of multi-

component devices. One approach to improve the sinterability of ceramics is to increase the powder reactivity via a reduction in particle size. It has been reported in many studies that nano-sized Y-TZP powders with weak agglomerates exhibit greatly enhanced sintering activity and thus sintering proceeds fast at relative low temperatures (<1100 °C).^{8–10} Another possible method is the presence of liquid phases during sintering via addition of sintering aids.^{11–13} However, addition of sintering aids can also lead to formation amorphous grain boundary phases and significant grain growth, which are undesired for several applications.

In the present work a significant enhancement in sintering activity of a 3Y-TZP nano-powder, without presence of liquid phase, was achieved by addition of 8 mol% of CuO nano-powder. Weakly agglomerated nanocrystalline 3Y-TZP and CuO powders prepared by wet-chemical synthesis techniques¹⁴ were used in this study. The sintering behaviour was analysed by means of dilatometer measurements, while microstructure was analysed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Zirconia phase transformation during sintering was investigated by means of high temperature X-ray diffraction. The sintering behaviour and zirconia phase transformation of the nano-powder composite are discussed in terms of reactions between CuO and 3Y-TZP grains.

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2. Experimental

2.1. Powder synthesis

A nanocrystalline powder of 3 mol% yttria stabilised tetragonal zirconia polycrystals (3Y-TZP) was prepared by a co-precipitation technique of metal chlorides, as described in detail elsewhere.¹⁵ An aqueous solution (pH $\sim$ 2) containing proper amounts of Zr^{4+} and Y^{3+} ions was added by means of a peristaltic pump to a concentrated aqueous ammonia (pH $\sim$ 14) solution. The ammonia solution was stirred vigorously and continuously with a top-mounted turbine stirrer. The resulting wet gel was washed chloride-free with distilled water/ammonia mixtures. Subsequently the precipitate was washed with ethanol to remove water. The gel suspended in ethanol, was then oven-dried overnight at 100 °C. The resulting amorphous powder was ground and sieved through a 180 μ m sieve, and subsequently calcined at 550 °C in stagnant air for 2 h. The proper composition of the 3Y-TZP powder was confirmed by an XRF (PW 1480, Philips) analysis. The calcined powder was then sieved through a 180 μ m sieve and stored in a desiccator.

A copper oxalate precipitation method was applied to prepare the nanocrystalline copper-oxide powders. Detailed procedure was described in.¹⁴ A Cu alcohol solution (0.5 M) was added at a controlled speed to an oxalic acid solution in alcohol (0.5 M) to form the copper oxalate complex precipitate. Oxalic acid was strongly stirred by a magnetic stirrer during addition of the Cu solution. The suspension was oven-dried overnight at 100 °C and then ground and sieved through a 180 μ m sieve. The sieved complex powder was calcined at 250 °C for 2 h. The resulting black powder was sieved again through a 180 μ m sieve and stored in a desiccator.

An 8 mol%-CuO doped 3Y-TZP composite powder was prepared by milling the proper amounts of 3Y-TZP and copper-oxide powder for 24 h in a polyethylene bottle, using ethanol and zirconia balls as milling media. The milled suspension was ultrasonically dispersed for 5 min and then oven-dried at 100 °C for 24 h. The dry cake of the composite powder was ground lightly in a plastic mortar and sieved through a 180 μ m sieve.

The nanocrystalline 3Y-TZP and copper oxide powders were characterised by XRD, BET as described elsewhere.¹⁴

2.2. Sintering behaviour study

Cylindrical green compacts of nanocrystalline 3Y-TZP powder and the composite powders were prepared by isostatic pressing at 400 MPa. The diameter and length of the compacts are 7–8 and 12–15 mm, respectively. The green densities (measured by the Archimedes' technique in mercury) of the compacts are 44–46% of the theoretical density of tetragonal zirconia. The sintering behaviour of the compacts was studied using a Netzsch 402E dilatometer in an oxygen flow. For all dilatometer measurements a three segments temperature program was applied, including heating from room temperature at 15 °C min⁻¹, holding at 1130 °C for 1 h, and cooling to room temperature at 5 °C min⁻¹. Linear shrinkage was recorded as function of time and temperature. The density as a function of temperature

was calculated from the green density and linear shrinkage data.¹⁶

2.3. Crystal structure analysis

Slices of 3Y-TZP and composites with dimensions of 10 mm $\times$ 8 mm $\times$ 0.5 mm were prepared by isostatic pressing followed by careful polishing with sand papers (silicon carbide paper, P# 1000). These slices were used for X-ray diffraction (XRD, X'Pert_MPD, PANalytical) analysis at various temperatures in order to investigate possible zirconia phase changes during sintering. During the XRD experiments, the samples were heated and cooled at 5 °C min⁻¹. At each measuring temperature the slice was held at that temperature for 15 min before measurement started. The volume fraction of monoclinic and tetragonal zirconia phases was calculated based on the peak intensities of $M[1\ 1\ 1]$, $M[\bar{1}\ 1\ 1]$ and $T[1\ 1\ 1]$ XRD signals using the relationship as proposed by Toraya et al.¹⁷

2.4. Microstructure characterisation

Scanning electron microscopy (SEM-EDX, Thermo NORAN Instruments) analysis was conducted on cross sections of the sintered samples. Prior to SEM experiments, the surfaces were carefully polished and thermally etched at 850 °C for 2 h. Transmission electron microscopy (TEM, CM30 Twin/STEM, Philips) analysis was carried out on the sintered CuO doped 3Y-TZP sample to investigate the grain boundary properties.

3. Results

3.1. Powder characteristics

The characteristics of the nanocrystalline 3Y-TZP and copper-oxide powders have been reported in details elsewhere.¹⁴ It was observed that the 3Y-TZP powder contains pure tetragonal zirconia particles with an equivalent diameter as calculated by the BET surface area (D_{BET}) of 10 nm. The CuO powder synthesised in this work has a D_{BET} of 50 nm and exhibits a multiphase composition including CuO, Cu₂O and metallic Cu.¹⁴ The specific amounts of those phases are not important for the sintering behaviour or zirconia phase changes of the CuO doped 3Y-TZP as treated in this work. During early stage heating both Cu₂O and Cu is oxidised to CuO phase below 350 °C as shown by thermogravimetric analysis of the copper oxalate complex, while sintering and zirconia phase changes have not started yet.

3.2. Sintering behaviour

Fig. 1 shows the relative density (corrected for weight loss and thermal expansion) and the linear densification rate ($d(\Delta L/L_0)/dt$) of the 8 mol% CuO doped 3Y-TZP nanocomposite as functions of temperature, during heating in an oxygen flow. The data of undoped 3Y-TZP were also shown in the figure for comparison. As can be seen in Fig. 1 the addition of nanocrystalline CuO drastically changes the sintering behaviour of nanocrystalline 3Y-TZP. In general it can be stated that sin-

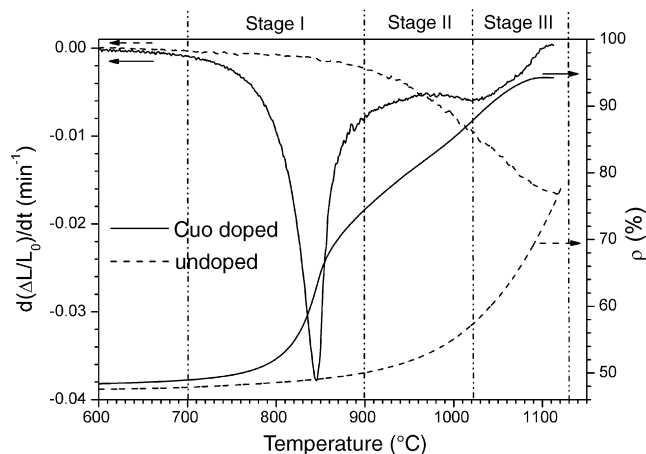


Fig. 1. Density and linear shrinkage rate as functions of temperature during heating. Solid lines are of 8 mol% CuO doped 3Y-TZP nano-powder composite; dashed lines are of undoped 3Y-TZP nano-powder compact.

tering of the CuO doped 3Y-TZP composite can be divided into three stages, e.g. stage I (700–900 °C), stage II (900–1020 °C) and stage III (1020–1100 °C).

In stage I it is shown that the addition of CuO decreased the onset temperature of densification of 3Y-TZP from 850 °C (undoped) to 700 °C (CuO doped). Shortly after the start of densification, the composite sample showed a drastic increase in densification rate until 850 °C. Within the next 50 °C temperature range (around 3 min of heating) the densification slowed down rapidly. After this sintering stage the density of the CuO doped sample was increased from 50% to 75%, while densification of the undoped 3Y-TZP did not started hardly in the same temperature range.

In sintering stage II densification of CuO doped 3Y-TZP proceeded at a relatively low rate. However, the contribution in this stage to the total densification is also significant (an increase from 75% to 90%) of the CuO doped sample was achieved in this sintering stage, indicating that sintering has almost been finished after heating at 15 °C min⁻¹ to around 1000 °C. In contrast, densification of the undoped 3Y-TZP sample just started in this temperature range and the density is only below 60%.

The densification of the CuO doped sample slowed down gradually in stage III since densification is almost finished in stage II. After the dilatometer experiment the CuO doped 3Y-TZP had a relative density of 96% (the presence of 80 vol% monoclinic zirconia phase in the sintered sample is taken into account for the calculation of theoretical density).

3.3. Microstructure and zirconia phase evolution of the CuO doped 3Y-TZP composite

Fig. 2 shows a SEM image of the cross-section surface of the CuO doped 3Y-TZP composite after the dilatometer experiment. The sintered composite exhibits a quite dense structure. However the grain size varies in a wide range from 200 nm to 1 μm, indicating that abnormal grain growth occurred during sintering. Occasionally some bright faceted grains are visible in the SEM image (as pointed out by the white arrow in Fig. 2). It

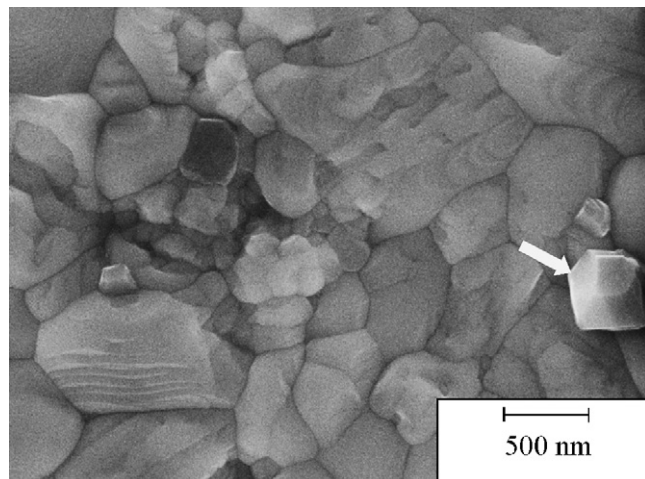


Fig. 2. Cross-section SEM image of 8 mol% CuO doped 3Y-TZP nano-powder composite sintered at 1130 °C for 1 h in an oxygen flow.

is revealed by EDX analysis that these faceted grains are almost pure CuO. As revealed by TEM analysis, the grain boundaries of the composite sample are clean (see Fig. 3). No amorphous phase can be observed in the grain boundary region or triple grain junctions. EDX analysis combined with TEM showed that copper oxide exists as crystalline particles with a diameter of 100–200 nm among the matrix of zirconia grains.

The volume fractions (V_M) of monoclinic zirconia in the CuO doped 3Y-TZP composite and the undoped 3Y-TZP are plotted as a function of temperature in Fig. 4. As can be seen from the figure, both CuO doped and undoped green compacts contain significant amounts of monoclinic zirconia, although they were prepared using a pure tetragonal zirconia powder. The presence of monoclinic zirconia in the green compacts was caused by the stress applied during polishing prior to XRD measurements. With increasing temperatures the monoclinic zirconia phase was reduced in both cases due to stress relaxation. Whereas the monoclinic zirconia disappeared in the undoped 3Y-TZP after the sample was heated to 950 °C, V_M of the CuO doped 3Y-TZP composite started to increase at 850 °C. Especially in

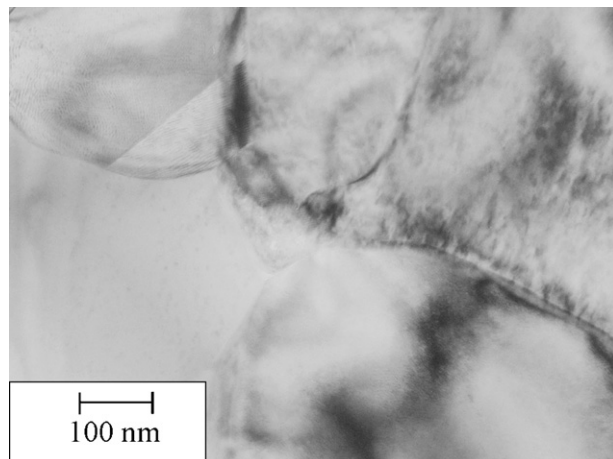


Fig. 3. TEM image of 8 mol% CuO doped 3Y-TZP nano-powder composite sintered at 1130 °C for 1 h in an oxygen flow.

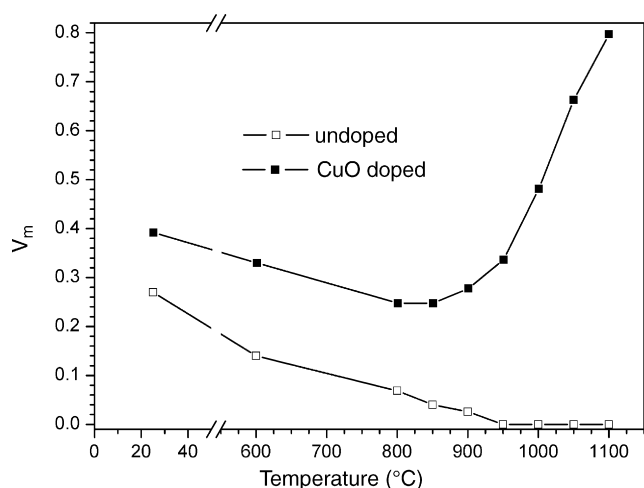


Fig. 4. Volume fraction of monoclinic zirconia as a function of temperature during heating. Solid square symbols are of 8 mol% CuO doped 3Y-TZP nano-powder composite; open square symbols are of undoped 3Y-TZP.

the temperature range of 900–1100 °C the monoclinic zirconia increases drastically from 30% to 80%, indicating some reactions extremely destabilises the tetragonal zirconia phase in this temperature range. After dilatometer experiment the CuO doped 3Y-TZP composite contains also around 80 vol% monoclinic zirconia, indicating that no zirconia phase transformation occurred during cooling. Correspondingly no volume expansion caused by zirconia phase changes was observed during, as was the case for a coarse-grained 0.8 mol% CuO doped 3Y-TZP sintered at 1400 °C.¹⁶

4. Discussion

4.1. Fast densification of CuO doped 3Y-TZP in sintering stage I

It has been reported that during sintering several reactions occur in the CuO doped Y-TZP systems,¹⁸ and those reactions have profound influences on densification behaviour of coarse-grained 0.8 mol% CuO doped 3Y-TZP ceramics.¹⁶ Basically the difference between sintering behaviours of undoped and CuO doped nanocrystalline 3Y-TZP systems as shown here in Fig. 1 can also be interpreted in terms of reactions occurring during heating.

The first effect of CuO addition on the sintering behaviour of 3Y-TZP is the fact that the onset temperature of densification is lower. This phenomenon was also observed in our previous studies on coarse- and nano-powder composites of 3Y-TZP doped with lower amounts of CuO (0.8 mol%).^{14,16} The low onset temperature can be attributed to the dissolution of CuO in the Y-TZP matrix by forming CuO-rich grain boundaries in the zirconia grains,^{18,19} which increases the ion mobility of zirconia grains and especially the grain boundary region.^{16,20} The higher ion mobility results in activation in sintering of the zirconia grains and therefore the onset of densification shifts towards lower temperatures.

The extremely fast densification rate of the CuO doped 3Y-TZP composite observed in sintering stage I is a very unique phenomenon. To our knowledge Y-TZP systems did not exhibit significant densification at such low temperatures (<900 °C) even when sintering aids were used. It is important to point out that in sintering stage I all the components in the composite studied here are in the solid phases. Therefore liquid-phase sintering kinetics, normally a reason of lower densification temperatures does not occur in this case. As discussed before the dissolution of CuO in the Y-TZP matrix significantly activates the sintering process by increasing the grain boundary diffusivity. This dissolution mainly takes place in the grain boundary region of zirconia. Therefore the area of Y-TZP grain boundaries per unit of volume as well as the Y-TZP/CuO contact area per unit volume are important for the dissolution and consequently for the activation of the sintering process. In the composite studied in this paper both Y-TZP and CuO grain size are on a nano scale. Additionally this composite contains a relatively large amount of CuO (8 mol%). Assuming the CuO grains are uniformly distributed among the 3Y-TZP matrix, it is obvious that the composite are possessing both a high Y-TZP grain boundary area and a high Y-TZP/CuO contact area. As a result of all these factors, large amounts of 3Y-TZP grains can significantly be activated for sintering by the dissolution of CuO in Y-TZP matrix in sintering stage I and correspondingly an extremely fast densification is possible.

Another result of the enhancement in ion mobility as caused by the strong CuO dissolution in the 3Y-TZP is the significant growth of zirconia grains. Although the Y-TZP/CuO contact area is relatively high in the nano-powder composite, still large amounts of Y-TZP grains are not in contact with CuO grains and so CuO dissolution did not occur for all Y-TZP grains. The large grains with a size up to 1 µm as shown in Fig. 2 are expected to be originally in contact with CuO grains. On the contrary, the Y-TZP grains that were not in contact with CuO shows a grain diameter of 100–200 nm, which is similar with the grain size of an undoped 3Y-TZP nano-powders sintered in the same way.^{8,14}

4.2. Zirconia phase evolution during sintering

The tetragonal to monoclinic (t–m) phase transformation of zirconia during heating was also observed in a previous study of a coarse powder composite of 0.8 mol% CuO doped 3Y-TZP.¹⁶ However, compared with the coarse powder composite, the t–m zirconia phase transformation in the nano–nano composite started at much lower temperatures (800 °C compared with 1100 °C) and proceeded more intensively. As discussed in our previous work¹⁶ as well as in other references,²¹ the t–m transformation of zirconia in CuO doped Y-TZP systems can be related to the reaction between the CuO and yttria as segregated to Y-TZP grain boundaries. According to the pseudo-binary phase diagram of the Y₂O₃–CuO system in air²² a reaction between Y₂O₃ and CuO takes place at elevated temperatures (>800 °C), resulting in the formation of an yttria-copper-oxide phase. As a result of this reaction in the CuO Y-TZP composite Y-TZP grains are depleted of yttria and tetragonal zirconia phase is destabilised. However this reaction occurs only to a

large extent when the material possesses sufficient Y-TZP/CuO contact area and significant yttria segregation to the grain boundaries. In the CuO-doped 3Y-TZP composite studied in this paper large amounts of Y-TZP/CuO contact are present as discussed above. The yttria segregation is actually a rate-limiting process of the reaction between CuO and yttria, and consequently controls the t–m phase transformation of zirconia. It has been shown that significant yttria segregation to Y-TZP grain boundaries occurs intensively above 850 °C.^{23,24} Therefore a significant reaction between Y₂O₃ and CuO and subsequently pronounced t–m phase transformation of zirconia started around this temperature as shown in Fig. 4. Heating up to 1100 °C results in the formation of 80% of monoclinic zirconia. After cooling to room temperature at the end of the sintering process also 80% of monoclinic zirconia is observed. So during cooling no further formation of monoclinic zirconia arises. This last phenomenon was also proven by the fact that during cooling no expansion was observed in dilatometer experiments.

5. Conclusions

The sintering behaviour of an 8 mol% CuO-doped 3Y-TZP nano-powder composite was investigated by means of dilatometer measurements. The nano-powder composite was prepared from 3Y-TZP and CuO powders with BET equivalent particle diameters of 10 and 50 nm, respectively. This nano-powder composite exhibits a low onset temperature of densification (750 °C) followed by an extremely fast densification at relatively low temperatures (<900 °C). This unique sintering behaviour was interpreted in terms of the dissolution of CuO in the 3Y-TZP matrix due to the large 3Y-TZP/CuO contact area per unit of volume in the nano-powder composite. This CuO dissolution also results in a strong grain growth during sintering.

High temperature XRD analysis revealed that a pronounced tetragonal to monoclinic phase transformation of zirconia occurs above 900 °C during heating. This phenomenon can be explained by the depletion of yttria in the Y-TZP grains, which is caused by the reaction between CuO and yttria as segregated from the Y-TZP grains resulting in a thermodynamically unstable tetragonal phase, which then transforms to the stable monoclinic structure. During cooling after sintering the ratio monoclinic/tetragonal zirconia does not change in these CuO/3Y-TZP nano/nano composites.

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References

- Garvie, R. C., Hannink, R. H. J. and Pascoe, R. T., Ceramic steel. *Nature*, 1975, **258**, 703–704.
- Garvie, R. C., Structural applications of ZrO₂-bearing materials. In *Advances in Ceramics*, Vol. 12: *Science and Technology of Zirconia II*, ed. N. Claussen, M. Ruhle and A. H. Heuer. The American Ceramic Society, Columbus, Ohio, 1984, pp. 465–479.
- Singhal, S. C., Advances in solid oxide fuel cell technology. *Solid State Ionics*, 2000, **135**, 305–313.
- Maskell, W. C. and Steele, B. C. H., Solid state potentiometric oxygen gas sensors. *J. Appl. Electrochem.*, 1986, **16**, 475–489.
- Wakai, F., Sakaguchi, S. and Matsuno, Y., Superplasticity of yttria-stabilized tetragonal ZrO₂ polycrystals. *Adv. Ceram. Mater.*, 1986, **1**, 259–263.
- Kerkwijk, B., García, M., van Zyl, W. E., Winnubst, L., Mulder, E. J., Schipper, D. J. and Verweij, H., Friction behaviour of solid oxide lubricants as second phase in α -Al₂O₃ and stabilised ZrO₂ composites. *Wear*, 2004, **256**(1–2), 182–189.
- Pasaribu, H. R., Sloetjes, J. W. and Schipper, D. J., Friction reduction by adding copper oxide into alumina and zirconia ceramics. *Wear*, 2003, **255**(1–6), 699–707.
- Theunissen, G. S. A. M., Winnubst, A. J. A. and Burggraaf, A. J., Sintering kinetics and microstructure development of nanoscale Y-TZP ceramics. *J. Eur. Ceram. Soc.*, 1993, **11**(4), 315–324.
- Durh, P., Villegas, M., Fernhndez, J. F., Capel, F. and Moure, C., Theoretically dense and nanostructured ceramics by pressureless sintering of nanosized Y-TZP powders. *Mater. Sci. Eng. A*, 1997, **232**, 168–176.
- Zhu, Q. and Fan, B., Low temperature sintering of 8YSZ electrolyte film for intermediate temperature solid oxide fuel cells. *Solid State Ionics*, 2005, **176**, 889–894.
- Boutz, M. M. R., Winnubst, A. J. A., Hartgers, F. and Burggraaf, A. J., Effect of additives on densification and deformation of tetragonal zirconia. *J. Mater. Sci.*, 1994, **29**, 5374–5382.
- Kimura, N., Okamura, H. and Morishita, J., Preparation of low-Y₂O₃-TZP by low-temperature sintering. In *Advances in Ceramics*, Vol. 24: *Science and Technology of Zirconia III*. The American Ceramic Society, 1988, pp. 183–191.
- Lawson, S., Gill, C. and Dransfield, G. P., The effects of copper and iron oxide additions on the sintering and properties of Y-TZP. *J. Mater. Sci.*, 1995, **30**(12), 3057–3060.
- Ran, S., Winnubst, A. J. A., Wiratha, W., Blank and Dave, H. A., Synthesis, sintering and microstructure of 3Y-TZP/CuO nano-powder composites”. *J. Eur. Ceram. Soc.*, 2006, **26**, 391–396.
- Groot Zevert, W. F. M., Winnubst, A. J. A., Theunissen, G. S. A. M. and Burggraaf, A. J., Powder preparation and compaction behaviour of fine-grained Y-TZP. *J. Mater. Sci.*, 1990, **25**(11), 3449–3455.
- Ran, S., Winnubst, A. J. A., Wiratha, W. and Blank, Dave H. A., Sintering behavior of 0.8 mol%-CuO-doped 3Y-TZP ceramics. *J. Am. Ceram. Soc.*, 2006, **89**(1), 151–155.
- Toraya, H., Yoshimura, M. and Somiya, S., Calibration curve for quantitative analysis of the monoclinic-tetragonal ZrO₂ system by X-ray diffraction. *J. Am. Ceram. Soc.*, 1984, **67**(6), C119–C121.
- Seidensticker, J. R. and Mayo, M. J., Thermal analysis of 3-mol%-yttria-stabilized tetragonal zirconia powder doped with copper oxide. *J. Am. Ceram. Soc.*, 1996, **79**(2), 401–406.
- Mayo, M. J., Seidensticker, J. R., Hauge, D. C. and Carim, A. H., Surface chemistry effects on the processing and superplastic properties of nanocrystalline oxide ceramics. *Nanostruct. Mater.*, 1999, **11**(2), 271–282.
- Raming, T. P., Winnubst, A. J. A., van Zyl, W. E. and Verweij, H., Densification of zirconia–hematite nanopowders. *J. Eur. Ceram. Soc.*, 2003, **23**(7), 1053–1060.
- Lemaire, L., Scholz, S. M., Bowen, P., Dutta, J., Hofmeister, H. and Hofmann, H., Effect of CuO additives on the reversibility of zirconia crystalline phase transitions. *J. Mater. Sci.*, 1999, **34**, 2207–2215.
- Gadalla, A. M. and Kongkachuichay, P., Compatible phases of the Y₂O₃–CuO–Cu₂O system in air. *J. Mater. Res.*, 1991, **6**, 450–454.
- Burggraaf, A. J., van Hemert, M., Scholten, D. and Winnubst, A. J. A., Chemical composition of oxidic interfaces in relation with electric and electrochemical properties. In *Reaction of Solid*, ed. P. Barret and L. C. Dufour, 1985, pp. 797–802.
- Theunissen, G. S. A. M., Winnubst, A. J. A. and Burggraaf, A. J., Segregation aspects in the ZrO₂–Y₂O₃ ceramic system. *J. Mater. Sci. Lett.*, 1989, **8**(1), 55–57.