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Sintering Behavior of 0.8 mol%-CuO-Doped 3Y-TZP Ceramics

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In recent years, 3 mol% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) doped with copper oxide has obtained increasing interest due to its enhanced superplastisity and good potential in tribological applications. In this work, the effect of addition of small amounts (0.8 mol%) of copper oxide on the sintering behavior of 3Y-TZP was studied using a dilatometer and high-temperature X-ray diffraction (XRD). A qualitative sintering model was established based on several reactions during sintering as indicated by thermal analysis and XRD. Some of these reactions remarkably retard densification and consequently result in low final density (86%) of the sample sintered at 1400°C in air. The reaction between molten Cu_2O and yttria as segregated to the Y-TZP grain boundaries at around 1180°C leads to the depletion of yttria from Y-TZP grains, which results in the formation of monoclinic phase during cooling. A relatively higher oxygen partial pressure can inhibit the dissociation of CuO to Cu_2O. This inhibition in dissociation is one of the reasons why a dense (>96%) 0.8 mol% CuO-doped 3Y-TZP ceramic can be obtained after sintering at 1400°C in flowing oxygen.

I. Introduction

Since the discovery of the transformation-toughening phenomenon in tetragonal zirconia-based ceramics, these materials have gained interests in industrial applications.[1] It has been shown that yttria-doped tetragonal zirconia polycrystals (Y-TZP) ceramics display extremely high values of bending strength and fracture toughness.[2,3] Due to their excellent mechanical properties and chemical inertness Y-TZP ceramics are increasingly considered for a wide range of structural applications such as extrusion dies, cutting tools, valve guides, etc.[4] In addition, fine-grained Y-TZP also exhibits a superplastic deformation property, which has opened up the possibility of using ceramics in ductile near net shape forming operations.[5]

In order to lower the sintering temperature, transition metal oxides like Fe_2O_3, Bi_2O_3,[6] or CuO[7] are often used as sintering additives. Moreover, addition of transition metal oxides also has important effects on physical properties of Y-TZP. It was reported that an addition of 0.25 wt% Fe_2O_3 or 0.07 wt% (0.1 mol%) CuO results in significant strength retention of Y-TZP ceramics after ageing in water or humid environment.[8] It is also well known that the addition of a small amount of CuO (<1 mol%) to Y-TZP strongly enhances the superplastic performance of zirconia ceramics.[9] Recently, tribological studies on 3 mol% yttria-stabilized tetragonal zirconia polycrystalline (3Y-TZP) ceramics showed that the addition of 1.8 mol% of CuO leads to a reduction of friction coefficient from 0.6 to 0.2 under dry sliding conditions.[10,11]

For the CuO-doped Y-TZP system, the special tribological and superplastic properties are strongly dependent on the fabrication process. The whole process from powder preparation to sintering procedure has a significant influence on the final ceramic microstructure and consequently its properties. In order to optimize the fabrication process, it is important to have knowledge of the effect of CuO on the sintering behavior. Detailed studies of the sintering behavior of CuO-doped Y-TZP systems are not easy to be found in literature. A thermal analysis of a 3Y-TZP powder doped with copper oxide as performed by Seidensticker and Mayo[12] has shown that several reactions occur in this system. The contribution of these several reactions to the sintering behavior of CuO-doped Y-TZP is not described yet.

In this work, the sintering behavior is studied of undoped and CuO-doped 3Y-TZP using a dilatometer. In order to investigate the influence of CuO as a second phase on the sintering of 3Y-TZP, such an amount of CuO (0.8 mol%) was chosen, which is slightly more than the solubility limit of CuO in the 3Y-TZP matrix (0.3 mol%).[12,13] The several effects of CuO addition to Y-TZP on sintering behavior, microstructure development, and zirconia phase evolution of these systems are discussed in terms of the several reactions, which may occur in the CuO Y-TZP system. These reactions during sintering are also interpreted by using among other things the thermal analysis experiments (differential thermal analysis (DTA)) as performed by Seidensticker and Mayo.[12] Furthermore, the influence of oxygen partial pressure on sintering behavior is described.

II. Experimental Procedure

Highly pure commercial 3Y-TZP (TZ3Y, Tosoh, Tokyo, Japan) and CuO powders (Aldrich Chemicals, Steinheim, Germany) were used as starting materials. The basic characteristics of the starting powders are listed in Table I. A powder mixture of 3Y-TZP with CuO was prepared by ball milling in ethanol for 24 h, using zirconia balls as milling medium. The CuO content was 0.8 mol% (0.5 wt%). The milled slurry was oven-dried at 80°C for 24 h and subsequently at 120°C for 8 h. The dry cake was ground slightly in a plastic mortar and sieved through a 180 μm sieve. Cylindrical compacts of the powder mixture and pure 3Y-TZP powder (milled in the same way as used for the mixture powder) were made by cold isostatic pressing at 400 MPa. The length and diameter of the compacts are 10–15 and 6–7 mm respectively. The green density of these compacts, measured by Achimedes technique in mercury, was 50%–52% of the theoretical density of tetragonal zirconia (6.09 g/cm^3).

The sintering behavior was studied using a Netzsch 402E dilatometer (Selb, Germany), in stagnant air or in an oxygen flow. Linear shrinkage was recorded as a function of time while the samples were successively heated by 2°C/min, hold for 2 h at 1400°C and finally cooled by 4°C/min. Assuming isotropic densification for all samples, the density (ρ in g/cm^3) as a function of temperature during the dilatometer experiments was calculated from the green density and the observed linear shrinkage of the specimens and corrected for thermal expansion of the sample using:

$$\rho = \frac{\rho_G}{\{1 - \Delta L/L_0 + \alpha(T - T_R)\}^3} \qquad (1)$$

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Table I. Basic Characteristics of Commercial Powders

Material	Molecular weight (g/mol)	Theoretical density (g/cm^3)	Particle size
3Y-TZP	126.3	6.09	30–40 nm
CuO	79.5	6.31	~5 μm

3Y-TZP, 3 mol% yttria-stabilized tetragonal zirconia polycrystals.

where ρ_G is the green density corrected for weight loss (due to removal of adsorbed water), $\Delta L/L_0$ is the observed linear relative shrinkage, T is the measured temperature, T_R is the room temperature, and α is the thermal expansion coefficient of the sintered body. α was determined using the linear shrinkage data during cooling assuming no densification during cooling. The final densities after the dilatometer experiment as calculated in this way were in good agreement with those measured by the Achimedes technique (in mercury).

The zirconia phase evolution during sintering was investigated by X-ray diffraction (XRD, X'pert_APD, PANalytical, Almelo, The Netherlands) analysis on a green compact at various temperatures in air. Prior to the XRD experiment the green compact was polished with abrasive paper (grade 1200) to a slice of 10 mm × 8 mm × 0.5 mm in dimensions. A heating rate of 5°C/min was used during the XRD experiment. The volume fraction of the monoclinic zirconia phase was calculated from the (111) reflections using the relationship proposed by Toraya *et al.*[14] Microstructures of the samples after dilatometer measurements were characterized using a scanning electron microscopy (SEM, JSM5800, JEOL, Tokyo, Japan). Grain sizes in the samples were determined by the linear intercept technique from SEM micrograph of polished and thermally etched (1100°C for 0.5 h) surfaces.[15] Elemental distribution of the sintered samples was analyzed by an energy-dispersive X-ray (EDX) (Thermo NORAN Instruments, Middleton, WI).

III. Results

(1) Sintering Behavior in Air

Figure 1 shows the relative density as a function of temperature of undoped 3Y-TZP and 0.8 mol% CuO-doped 3Y-TZP during dilatometer tests in air. The relative density was calculated by using Eq. (1), while for the theoretical density the value of undoped 3Y-TZP (6.09 g/cm^3) was used. The undoped 3Y-TZP shows a gradual increase in density as a function of time/temperature. The densification curve of CuO-doped system indicates large differences during sintering, if compared with the undoped 3Y-TZP. CuO-doped 3Y-TZP starts to densify at a lower temperature (850°C compared with 950°C for 3Y-TZP). During subsequent heating several changes in densification occur for the CuO-doped system among which the sudden change at about 1200°C is the most remarkable. At this temperature densification was retarded significantly. During cooling, a sudden decrease in relative density, which comes from a volume expansion, can be observed clearly at around 615°C for the CuO-doped system. This expansion is related to the phase transformation from tetragonal to monoclinic zirconia. XRD analysis of the surface of this CuO-doped 3Y-YZP ceramic after sintering shows about 55 vol% monoclinic zirconia, while the undoped 3Y-TZP sample contains 100% tetragonal zirconia. This is in good agreement with the work of Lemaire *et al.*[16] and Hayakawa *et al.*,[17] who observed that an addition of more than 0.3 mol% of CuO results in the formation of monoclinic zirconia after sintering.

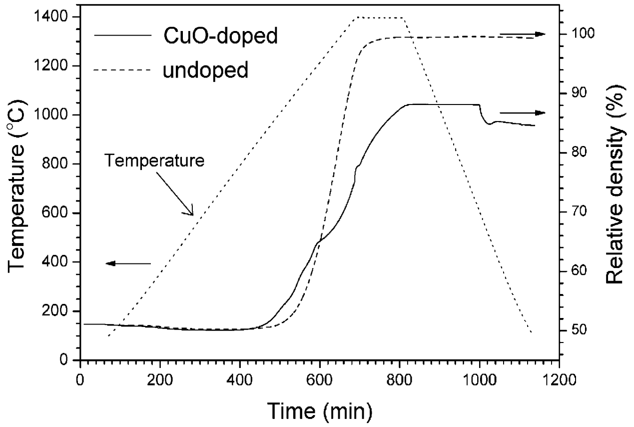

Fig. 1. Desification behavior of pure 3 mol% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) and CuO-doped 3Y-TZP during sintering in air.

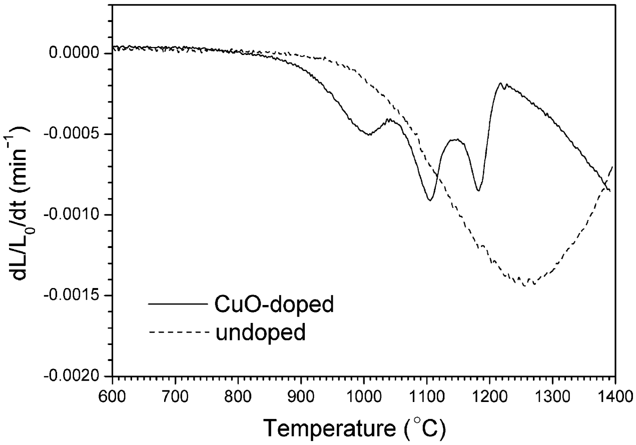

Fig. 2. Relative shrinkage rate of undoped 3 mol% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) and CuO-doped 3Y-TZP during sintering in air.

From Fig. 1 it can be seen that the total shrinkage of the CuO-doped sample is much less than that of the undoped one. The relative densities of the samples after sintering are respectively 86% and 99% of the theoretical one. For the case of CuO-doped 3Y-TZP the presence of monoclinic zirconia is taken into account for calculating the theoretical density (5.87 g/cm^3).

For a better understanding of the differences in densification during heating, the densification rate is considered. A measure of the densification rate is the relative linear shrinkage rate as depicted in Fig. 2. The undoped 3Y-TZP sample exhibits only one maximum in densification rate at 1280°C indicating normal densification behavior during the whole sintering process. For the CuO-doped sample several maximums during heating are visible, respectively at 1010°, 1105°, and 1185°C (Fig. 2). These variations in densification rate are caused by several reactions during heating and will be discussed in later sections.

After the dilatometer experiment in air, several small cracks of some millimeters in size were visible by eye on the surface of the CuO-doped sample. These cracks could be caused by stresses generated by the tetragonal to monoclinic phase transformation. Figure 3 shows an SEM image of a polished cross-section of the CuO-doped sample after the dilatometer experiment in air. It is clearly visible in the SEM picture that the sample contains many homogeneously distributed irregular pores with sizes up to 2 μm.

The grain size of Y-TZP phase is less than 1 μm, indicating that the grain growth of Y-TZP was not significantly large during sintering and is about the same for pure 3Y-TZP systems.

(2) Sintering Behavior in Oxygen

Dilatometer measurements on undoped and 0.8 mol% CuO-doped 3Y-TZP compacts were also conducted under a flowing oxygen stream. For the undoped 3Y-TZP, no remarkable influence of oxygen partial pressure on sintering behavior was found.

For the CuO-doped sample, the relative density curve is shown in Fig. 4. If compared to the CuO-doped sample sinte-

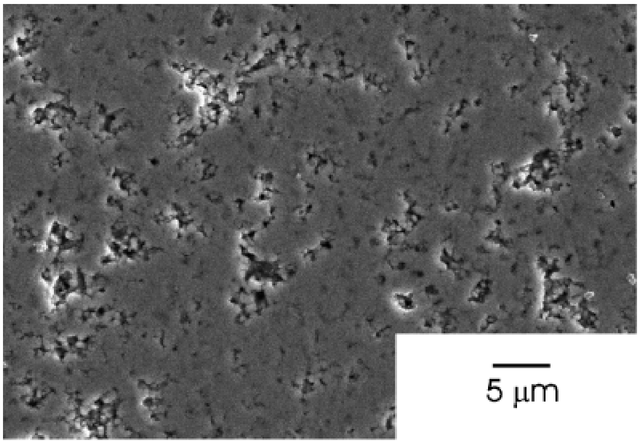

Fig. 3. Cross-section scanning electron microscopy image of a polished CuO-doped 3 mol% yttria-stabilized tetragonal zirconia polycrystals sintered in air.

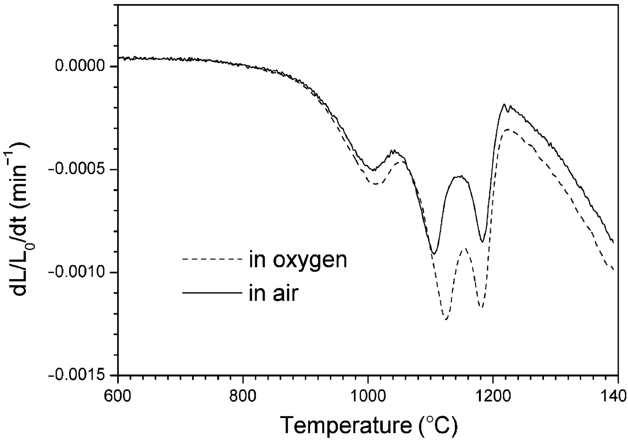

Fig. 5. Relative shrinkage rate of CuO-doped 3 mol% yttria-stabilized tetragonal zirconia polycrystals during sintering in air and flowing oxygen.

red in air, the sample sintered in oxygen showed similar changes in densification, but the total shrinkage is much higher. After the dilatometer experiment in oxygen, the sample achieved a relative density of 96% (the presence of monoclinic zirconia is taken into account for calculating the theoretical density). During cooling of this sample an expansion can be observed, indicating again a phase transformation from tetragonal to monoclinic zirconia. The difference with the air-sintered sample is the shift of the expansion during cooling to 550°C (115°C lower). XRD analysis shows that the sample sintered in oxygen contains the same amount of monoclinic zirconia as the sample sintered in air (about 55 vol%).

The influence of oxygen partial pressure on the densification rate can be seen from Fig. 5. This figure shows the relative linear shrinkage rate of the CuO-doped 3Y-TZP samples during heating in stagnant air and flowing oxygen. Generally all three maximums in densification rate as appeared during sintering in air are also present while sintering in flowing oxygen. In both cases, the temperature and intensity of the first maximum in densification rate (at 1000°C) are similar. However, the second maximum (at 1125°C in the case of oxygen) was delayed remarkably by the oxygen atmosphere, and has a relative stronger intensity as compared with the case in air. For the third maximum (at 1185°C) in densification rate, the influence of oxygen partial pressure was relatively less. After the dilatometer experiment in flowing oxygen, the sample looks good without visible cracks on the surface. SEM analysis of a polished cross-section of this sample showed a much denser structure if compared with the sample sintered in air (cf., Figs. 6 and 3). Only few small pores with sizes less than 1 μm can be observed from the SEM picture in Fig. 6. Beside this, many homogeneously distributed dark dots can be observed on this cross-section. EDX analysis indicated that these dark spots consist of a Cu-rich phase, while in the lighter areas almost no copper was detected.

(3) *Zirconia Phase Evolution During Heating in Air*

XRD analysis at various temperatures in air showed that both tetragonal and monoclinic zirconia phases are present in the CuO-doped 3Y-TZP system and that phase transformations occur while heating. Based on the XRD patterns, the volume fraction of these two phases can be calculated using the method as proposed by Toraya *et al.*[14] In Fig. 7, the volume fraction of monoclinic zirconia phase is plotted as a function of temperature. These results show that the green compact contains more than 35 vol% of monoclinic zirconia although it was made from pure tetragonal 3Y-TZP powder. This presence of monoclinic zirconia was caused by the tensile stress applied on the sample during polishing prior to the XRD experiment. With increasing temperature monoclinic zirconia gradually transforms to tetragonal zirconia due to the relaxation of tensile stress until it almost disappears at 800°C. However, at around 1100°C the tetragonal zirconia starts to transform back to monoclinic phase, indicating a reaction, which destabilizes the tetragonal zirconia phase at this temperature. Above 1200°C monoclinic zirconia transforms to the tetragonal phase again because thermodynamically tetragonal zirconia becomes the stable phase in this temperature region.

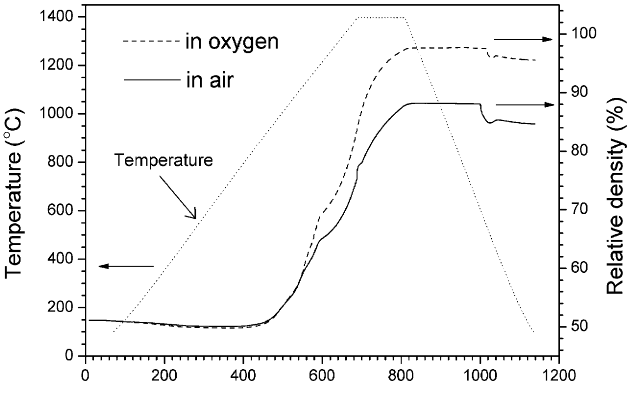

Fig. 4. Desification behavior of CuO-doped 3 mol% yttria-stabilized tetragonal zirconia polycrystals during sintering in air and flowing oxygen.

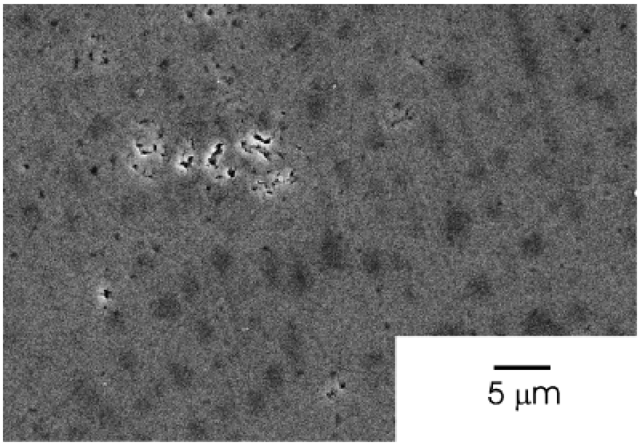

Fig. 6. Cross-section scanning electron microscopy image of a polished CuO-doped 3 mol% yttria-stabilized tetragonal zirconia polycrystals sintered in flowing oxygen.

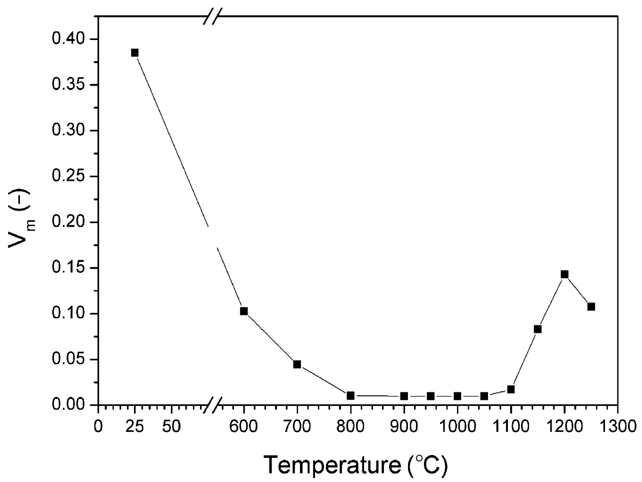

Fig. 7. Volume fraction of monoclinic zirconia in the CuO-doped 3 mol% yttria-stabilized tetragonal zirconia polycrystals as a function of temperature during heating in air.

IV. Discussion

(1) Effect of the Addition of CuO on the Densification Behavior of 3Y-TZP

It is shown that addition of a relative small amount of CuO (0.8 mol%) leads to several sintering stages during densification of 3Y-TZP (see Figs. 2 and 5). Generally, these changes in densification rate can be explained in terms of reactions between CuO and 3Y-TZP. These reactions will now be treated for the system sintered in air (see Fig. 2). First the onset for densification at lower temperature (850°C compared with 950°C for 3Y-TZP) will be discussed. It is known from literature that 0.3 mol% of CuO can dissolve in the Y-TZP matrix by forming a Cu-enriched grain-boundary layer of 1–2 nm in thickness.[12,13] DTA as performed by Seidensticker and Mayo[12] on a 3 mol% CuO-doped 3Y-TZP powder showed a small exothermic peak around 850°C, which was not present after re-heating the powder system.[12] It seems that this exothermic signal can be attributed to dissolution of CuO in Y-TZP. During this dissolution, the ion mobility in the 3Y-TZP grains and especially in the grain boundary region increases. This high ion mobility or ion diffusivity can be related to a high grain-boundary diffusion, which results in a higher densification rate,[18] and consequently leads to a start of densification at a lower temperature. If the dissolution proceeded completely, 0.3 mol% of CuO would have been dissolved in the Y-TZP matrix while 0.5 mol% of CuO remained as a separate phase.

At 1010°C, the densification rate slows down slightly. DTA as performed by Seidensticker and Mayo[12] on a 3 mol% CuO-doped 3Y-TZP powder showed an exothermic peak at around 1000°C during the first round of heating which is not present on reheating. The authors did not explain what reaction happens here. Nevertheless, this irreversible reaction is likely corresponding the decrease in densification at 1010°C as observed in this work.

After the first decrease in densification rate, further solid-state sintering starts at 1040°C as indicted by the increase in shrinkage rate (Fig. 2). However, at around 1100°C, the densification rate drops rapidly. High-temperature XRD analysis shows that a phase transformation from tetragonal to monoclinic zirconia starts at this temperature (see Fig. 7). The cause of this phase transformation will be discussed later. At first sight one might expect that the decrease in densification rate in this temperature region is simply caused by the volume expansion of zirconia grains (i.e., expansion of the zirconia lattice) resulted from the phase transformation. However, calculations based on the volume fraction of monoclinic zirconia indicate that the contribution of phase transformation to the overall sample volume change is less than 0.2% and therefore negligible if compared to the sintering process in the corresponding temperature range (1100°–1150°C). This is an indication that there must be another reaction, which contributes to the strong decrease in densification in this sintering stage. We propose that this phenomenon is caused by the dissociation of CuO.

It is shown that at 1030°C CuO starts to dissociate to Cu_2O while O_2 is released.[12] From the molecular weight and theoretical densities of CuO and Cu_2O, it can be calculated that the volume of a formed Cu_2O particle is 12% less than that of a CuO particle. As a result of this shrinkage of the copper oxide particles, pores are formed or grow rapidly. Considering the relative large particle size of CuO in the starting powder ($\sim$5 μm), one can see that large pores with diameter up to 200 nm could be formed due to the rapid volume shrinkage of the copper oxide particles. The grain size of Y-TZP after this sintering stage is only around 60 nm.[19] So the pores generated by the dissociation of CuO are about three times larger than the zirconia grains (the main phase in the composite), meaning a pore/grain size ratio of 3. It has been shown that pores tend to grow instead of shrink when the pore/grain size ratio exerts a certain value.[20] This critical ratio normally is less than 1. Subsequently, those large pores are difficult to be removed by normal solid-state sintering. The presence of the large pores with sizes up to several micrometers in the sample after sintering in air, as shown in the SEM picture (Fig. 3), is an evidence of pore growth during sintering. In conclusion, the reduction in densification, which starts at 1100°C, can likely be ascribed more to a mechanism related to CuO dissociation and not to the phase transformation of tetragonal to monoclinic zirconia, which also occurs in this temperature regime.

Pure Y-TZP does not exhibit a phase transformation from tetragonal to monoclinic zirconia while heating at these temperatures. The effect of CuO on this phase transformation will now be discussed. Lemaire *et al.*[16] observed in their study that after sintering in air of a CuO-doped Y-TZP sample a large amount of monoclinic zirconia was formed as well as an $Y_2Cu_2O_5$ sec phase. According to the pseudo-binary phase diagram of the Y_2O_3–CuO system in air[21] a reaction between Y_2O_3 and CuO takes place above 900°C, resulting in the formation of an yttria–copper-oxide phase. Another phenomenon is that after a temperature treatment above 900°C yttrium segregates to the grain boundaries of Y-TZP.[22,23] It was proposed by Lemaire *et al.*[16] that the yttria, as segregated to the Y-TZP grain boundaries, reacts with CuO to form the new reaction product ($Y_2Cu_2O_5$) resulting in zirconia grains having not sufficient yttria to stabilize the tetragonal phase. This explanation seems to be reasonable for the case treated in this work as well. Due to the few number of contact zones between Y-TZP and CuO grains in this temperature range (<1% yttria grains are in contact with CuO), the process described here proceeds rather limited so that only small amounts of tetragonal zirconia (<10%) transforms to monoclinic at a temperature below 1130°C.

Above 1130°C Cu_2O starts to melt,[12] resulting in a drastic change in sintering behavior. The first phenomenon observed is the increase in densification rate at this temperature as shown in Fig. 2. Liquid-phase sintering results in an enhancement in densification if the molten Cu_2O wets the Y-TZP grains well. On the other hand, the redistribution of molten copper oxide results in a larger contact area between Y-TZP and copper oxide. This increase in contact area leads to a more intensive reaction between copper oxide and yttria as segregated to Y-TZP grain boundaries. Moreover, after the melting of Cu_2O the reaction proceeds in a solid-liquid manner, while the reaction product also exists in a liquid form. It is expected that this solid-liquid reaction (>1130°C) proceeds much faster if compared to the solid–solid reaction between Cu_2O grains and yttria on the Y-TZP grain boundaries (<1130°C). DTA experiments as performed by Seidensticker and Mayo[12] showed an intensive broad endothermic peak above the melting temperature of Cu_2O, which they ascribed to the solid-liquid reaction as also discussed here. As a result of the further reaction between molten Cu_2O and yttria as segregated to the grain boundaries, more tetragonal zirconia is destabilized and transforms to monoclinic phase in this temperature range (1150°–1200°C, see Fig. 7). Above 1200°C the solid–liquid reaction can still proceed and more Y-TZP grains get depleted in yttria. The amount of monoclinic zirconia, however, decreases above 1200°C (Fig. 7) because tetragonal zirconia becomes the thermodynamically stable phase. During cooling all "depleted" zirconia grains transform to the monoclinic phase as indicated by the sudden volume expansion at 615°C (see Fig. 1).

The solid–liquid reaction and/or its liquid products (a yttria–copper oxide phase) seem to be detrimental for densification and result in a drastic decrease in densification rate at around 1180°C. One of the possible explanations for this phenomenon is that the newly formed liquid yttria-copper-oxide phase wets the Y-TZP grains less than molten Cu_2O.

(2) Effect of Oxygen Partial Pressure

All three densification rate maximums as appeared in the case of sintering in air, are also present in the case of sintering in flowing oxygen (Fig. 5). This is an indication that all the reactions, which occur during sintering in air also take place during sintering under a higher oxygen partial pressure. The most obvious effect of a higher oxygen partial pressure on sintering is the fact that the second decrease in densification rate starts at 1125°C, while during sintering in air densification in this temperature regime retards at 1100°C (see Fig. 5). It is stated in the discussion as given that dissociation of CuO to Cu_2O starts at 1040°C. This reaction can be expressed as follows:

$$4\mathrm{CuO}(s) \Leftrightarrow 2\mathrm{Cu_2O}(s) + \mathrm{O_2}(g) \qquad (2)$$

Judging from this equilibrium reaction, it is clear that this reaction proceeds slower to the right as a function of temperature under a higher oxygen partial pressure (oxygen flow compared with air). Obviously, the formation or evolution of pores due to this reaction takes place slower too. Additionally, because the temperature of this dissociation reaction is close to the melting point of copper oxide, mechanisms like rearrangement of Y-TZP grains and especially viscous flow can take place. The delay of dissociation of CuO allows the Y-TZP grains rearrangement and viscous flow to proceed more effectively to fill the pores. As a result, the size of the pores formed in this sintering stage can be significantly smaller if compared with the case of sintering in air. Although the pores size was still sufficiently large to inhibit densification as indicated by the second decrease in densification rate (Fig. 5), probably most of those pores were able to be removed in further sintering, especially while a liquid phase is present (above 1130°C). This is confirmed by the SEM picture of the sample after sintering in flowing oxygen (Fig. 6), which only shows few small pores.

V. Conclusions

A small amount of CuO addition leads to a remarkable change in densification behavior of 3Y-TZP. Several reactions occur during sintering which can be beneficial or detrimental for densification. The following sintering stages are discerned:

(1) The starting temperature of densification is lowered due to the dissolution of CuO in the Y-TZP matrix.

(2) A solid-state reaction at around 1000°C retards densification slightly.

(3) Dissociation of CuO to Cu_2O starts at 1040°C. Large pores can be formed when this reaction proceeds too fast. The formation of large pores retards densification remarkably and consequently leads to a low density and a poor microstructure of the 0.8 mol% CuO-doped 3Y-TZP sample after sintering in air.

(4) A higher oxygen partial pressure can slow down this dissociation of CuO. The 0.8 mol% CuO-doped 3Y-TZP sintered under a relatively high oxygen partial pressure (in flowing oxygen) has a density of 96%.

(5) While the Cu_2O starts to melt at 1130°C, densification is enhanced due to the presence of a liquid phase.

(6) After the melting of Cu_2O, a solid–liquid reaction between molten Cu_2O and yttria as segregated from the Y-TZP grains results in the decrease in densification rate at 1180°C. This reaction also leads to depletion of yttria from Y-TZP grains, and consequently destabilizes the tetragonal phase of zirconia.

(7) Both CuO-doped samples sintered in air and flowing oxygen contain 55 vol% of monoclinic zirconia while the undoped sample contains 100% tetragonal zirconia after sintering.

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