Effect of CuO additives on the reversibility of zirconia crystalline phase transitions

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We have studied the influence of the differents atmospheres on the sintering of CuO-doped-zirconia ceramics. After an annealing treatment in a reducing atmosphere, we have found nanoparticles of metallic copper in triple points and in the grains of the sintered zirconia. Furthermore, the influence of the intergranular $Y_2Cu_2O_5$ phase on the tetragonal to monoclinic phase transition and the crystalline structure of zirconia is discussed with respect to results obtained from X-ray diffraction, differential thermal analysis, Raman spectroscopy and High Resolution Transmission Electron Microscopy. © *1999 Kluwer Academic Publishers*

1. Introduction

Zirconia and ZrO_2 containing materials find a wide range of applications in foundry refractories, ceramics, abrasives and paint pigments. Tough, wear resistant, zirconia has been developed for applications such as extrusion dies, piston caps, and machinery wear parts amongst others [1]. Due to their excellent mechanical properties [2, 3] and high sinterability, yttria-doped tetragonal zirconia polycrystalline materials are often preferred in structural applications. ZrO_2 undergoes at least three crystallographic modifications upon cooling from a melt. At 2680 °C it is a cubic phase which crystallizes from the melt and transforms to a tetragonal phase at 2300 °C which in turn transforms to the monoclinic form between 950 and 1150 °C [4]. The insertion of Y_2O_3, CaO, MgO or Ce_2O_3 into the crystal structure is known to stabilize the high temperature phases of zirconia even at low temperatures [5]. The addition of a mixture of oxides to zirconia, which are transformed into a glassy phase after the heat treatment, further enhances densification of zirconia by wetting the grains and by increasing the grain-boundary diffusion. Transmission Electron Microscopy (TEM) studies [6, 7] of a zirconia microstructure show that the glassy phase is located in grain-boundaries and triple points: the higher the amount of glassy phase in the mixture, the larger are the triple points, while the thickness of the grain-boundaries are relatively constant ($1 < t$ (nm) < 3). The presence of copper oxide in the intergranular glassy phase also changes the crystalline structure of zirconia. It has been proposed that zirconia reacts with CuO to form a low melting point eutectic phase along the grain boundaries which increases the overall forming rate of 3Y-TZP [8]. However Seidensticker *et al.* [9] showed that the CuO reacts with the Y_2O_3 to form $Y_2Cu_2O_5$ after the composition in the grain boundaries

reach the CuO solubility limit. It has also been reported in a study on the chemical analysis of sintered zirconia microstructures by XPS [10], that copper is present as Cu^{++} in the grain-boundary glassy phase.

In order to understand the role and whereabouts of Cu in zirconia ceramics, we have studied both the sintering additive system looked at the effects on the sintering of zirconia ceramics themselves. The characterization of the intergranular phases in zirconia ceramics is rendered difficult because of the low fraction and fine structure (<3 nm); therefore in order to study effects of copper additions to the sintering additive mixture Y_2O_3, SiO_2, Al_2O_3 work was initially carried out in this system alone. After a heat treatment, the mixture of oxides Y_2O_3, SiO_2, Al_2O_3 and CuO is transformed in a glassy phase.

Here we report on the effect of annealing of the sintering additive (Y_2O_3, SiO_2, Al_2O_3 and CuO) and CuO-doped-zirconia pellets in both oxidizing (air) and reducing (N_2/H_2) atmospheres. We discuss in detail the changes in the valency of the copper ion upon varying the annealing atmosphere. From the experimental results we will discuss the question of the location of copper in the zirconia ceramics and the influence of the copper containing crystalline phases present in the grain boundaries and the triple points.

2. Experimental procedure

The mixture of zirconia stabilized with 3 mol % of Y_2O_3 (TZ-3YS, Tosoh Co, Japan) with the sintering additive (Y_2O_3, Al_2O_3, SiO_2, CuO) was attrition milled in an alumina jar with zirconia milling media in ethanol for half an hour. The percentage of sintering additive mixed with zirconia is fixed at 1 wt % while the percentage of CuO was varied, 0; 0.1; 0.18; 0.25

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and 0.45 wt % of TZ-3YS. The milled slurries were dried and uniaxially cold pressed. Dilatometric measurements (Setaram 2050) were carried out on each composition at 1500 °C for 1 h in air. An annealing treatment under N_2/H_2 (92/8) atmosphere was made on all the sintered samples.

The phase identification and the measurement of the lattice parameters were determined by X-ray diffraction (Kristalloflex 805, Siemens) and by Raman spectroscopy (Dilor XY 800). The determination of phase transformations of the glassy phase doped with copper were made by differential thermal analysis (Setaram 2050). Microstructures were characterized by SEM (Cambridge Instruments, S360) and by TEM (JEM 100 C). Chemical composition analysis of the microstructure were characterized by XPS (Perkin Elmer, PHI 5500) and HRTEM (JEM 4000 EX). For the XPS studies, both polished surfaces and fractured surfaces of samples with a high dopant concentration (0.9 wt % CuO) were prepared in order to be above the detection limit of the apparatus for copper.

Differential thermal analysis (DTA) studies were carried out exclusively with the glassy phase i.e. SiO_2-Al_2O_3-Y_2O_3, with varying concentrations of CuO dopant under similar conditions utilized for the preparation of CuO-doped-zirconia ceramic samples [$10°$/min until 1500 °C (1 h) and 10 °C/min until 20 °C] in order to study the influence of CuO on the intergranular vitreous phase in zirconia ceramics. The concentration of CuO in the glassy phase was chosen such so as to keep the proportion of copper as used for the sintering additive mixture. Thermal analysis were also made on a sample without any CuO additive in order to compare the results obtained from the doped samples.

3. Results and discussion
3.1. Location of CuO in sintered zirconia
Formation of the glassy phase from the oxide mixture does not take place in the initial thermal cycle but several thermal treatments need to be carried out before the characteristic peaks of the glassy phase can be observed in the DTA curve (Fig. 1). The shape of the curves are very similar to a typical DTA curve for a
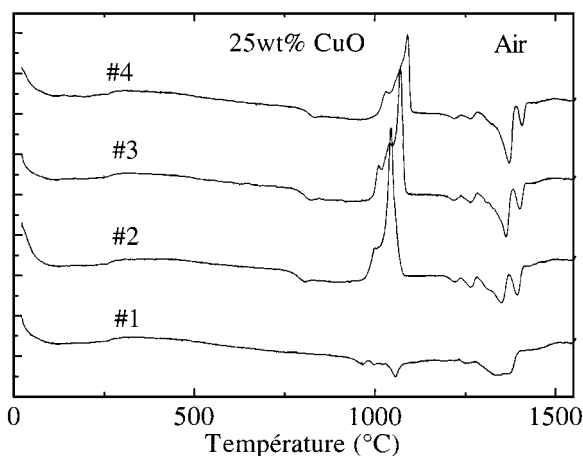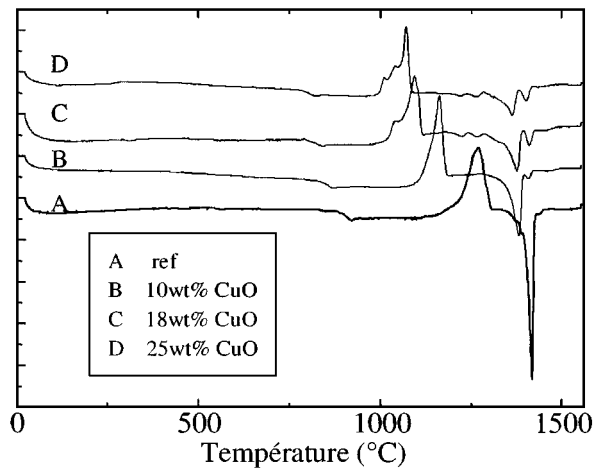

Figure 2 Thermal analysis of the glassy phase SiO_2-Al_2O_3-Y_2O_3 doped with various amounts of CuO (0, 10, 18 and 25 wt %).

glass, where distinct regions related to a vitreous transition T_g, a crystallization and melting can be observed. For phases doped with 18 wt % CuO or higher, we observe several peaks related to the crystallization and melting, suggesting the presence of several different crystalline phases. They are still evolving even after 4 cycles indicating neither a steady (equilibrium) state or glassy phase composition has been achieved. As the CuO concentration increases, the peaks shift significantly towards lower temperatures (from 1250 to 1050 °C for the crystallization) as shown in Fig. 2. X-ray diffraction of these differents compositions reveal the presence of $Y_2Cu_2O_5$.

X-ray diffraction analysis were carried out to determine the lattice parameters of zirconia for samples prepared with different CuO (0, 0.1, 0.18, 0.25, 0.45 wt %) concentrations (Fig. 3). As shown in Fig. 3, no substantial change in the lattice parameters were observed. XPS analysis was carried out on a fractured copper oxide doped zirconia sample. Supposing that the fracture is intergranular, we studied the intergranular glassy phase. The analysis reveals the presence of copper in the glassy phase (Fig. 4). Similar measurements on a polished ceramic sample (CuO-doped-zirconia) does not reveal the presence of any copper.

The constant lattice parameters with different dopant concentrations and the XPS results, suggest that copper
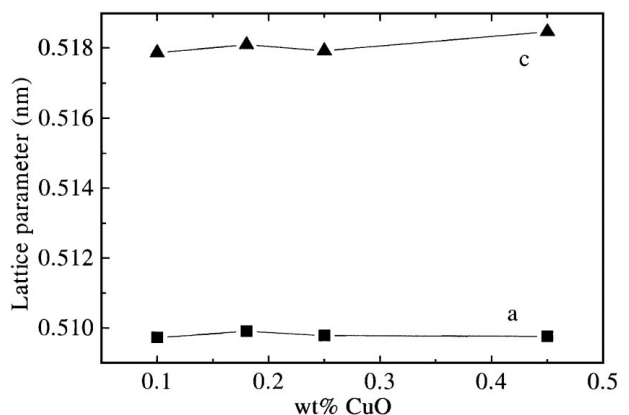

Figure 1 Cyclic thermal analysis of the glassy phase SiO_2-Al_2O_3-Y_2O_3 doped with 25 wt % CuO.

Figure 3 Lattice parameters of zirconia doped with differents amount of CuO (0.1, 0,18, 0.25 and 0.45 wt %).
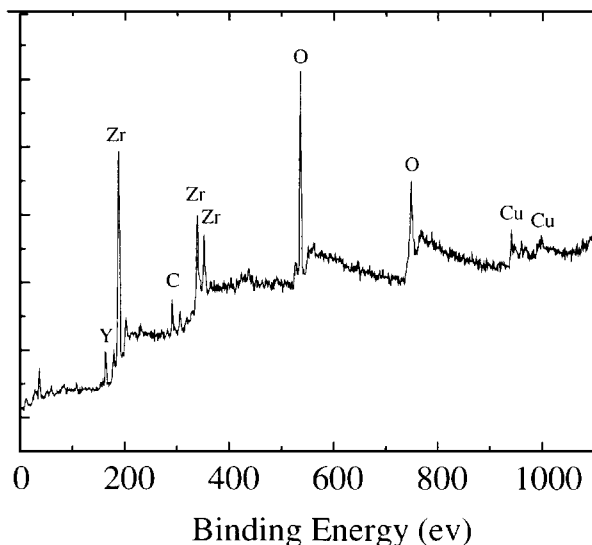
Figure 4 XPS data analysis of a fractured 0.9 wt % CuO-doped-zirconia.
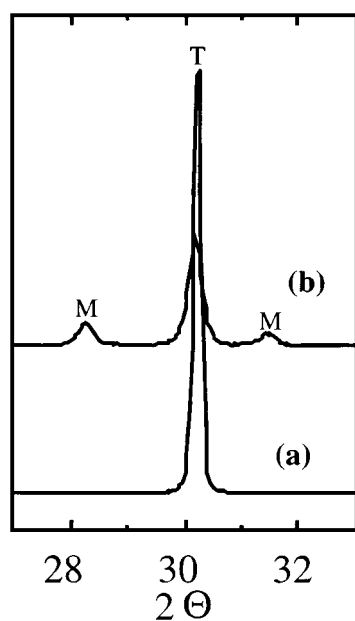

Figure 5 X-ray diffraction of sintered CuO-doped-zirconia showing the transformation from (a) tetragonal to some (b) monoclinic + tetragonal form with higher dopant content.

is not dissolved in the zirconia grains but is present in the grain boundary region and reacts with the grain boundary glassy phase consisting of SiO_2-Al_2O_3-Y_2O_3. X-ray diffraction measurements of sintered zirconia doped with different amounts of CuO show that for a small amount of copper oxide (<0.3 wt %), only the tetragonal (T) phase is observed, while for a higher amount of dopants, a small amount of the monoclinic form (M) can also be observed (Fig. 5). Chaim et al. [11] have argued that yttria migrates from grains into grain-boundaries by various diffusion processes during sintering. The grains which are deficient in yttria transform into the monoclinic phase, while the yttria rich grains become cubic. The same conclusion was reached by Nauer [12] while studying the role of impurities on the migration of yttria in grain boundaries of zirconia during sintering. In the present study, the copper dopant may influence the concentration of yttria in

the grain boundaries as well as in the grains. We assume that ZrO_2 is not dissolved in the triple points or grain boundaries after the sintering. The only thermodynamically stable phase of Y_2O_3 and CuO in air at ambient temperature is $Y_2Cu_2O_5$ [13]. Since a certain amount of Y_2O_3 is necessary for reaction with all the CuO available in the ceramic, this yttria may be obtained from the vitreous phase in the triple points. Thus, when the CuO dopant concentration is greater than Y_2O_3 (concentration needed for the $Y_2Cu_2O_5$ formation in the glassy phase), the deficiency in the yttria is fulfilled by the migration of Y_2O_3 from the zirconia grains. If the amount of Y_2O_3 lost from the grains to react with the CuO is sufficiently high there may no longer be enough Y_2O_3 to stabilize the tetragonal phase and monoclinic grains can appear on cooling.

TEM was carried out on a sample with 0.45 wt % CuO doped zirconia ceramic. The contrast features in the grains are due to strain arising from the thermal treatment and inhomogenities in localized chemical compositions within the grains (Fig. 6a). The martensitic transformation T → M of CuO-doped-zirconia is indicated in the micrograph (Fig. 6b) characterized by the presence of typical twins that arise from the shearing displacement of zirconium ions during the phase transformation. Irrespective of the amount of vitreous phase of additives in the CuO-doped-zirconia ceramics, the thickness of the grain boundary region remains unchanged (2 to 3 nm) while the triple points increase in size with increasing vitreous phase content. A typical triple point is shown in Fig. 6c.
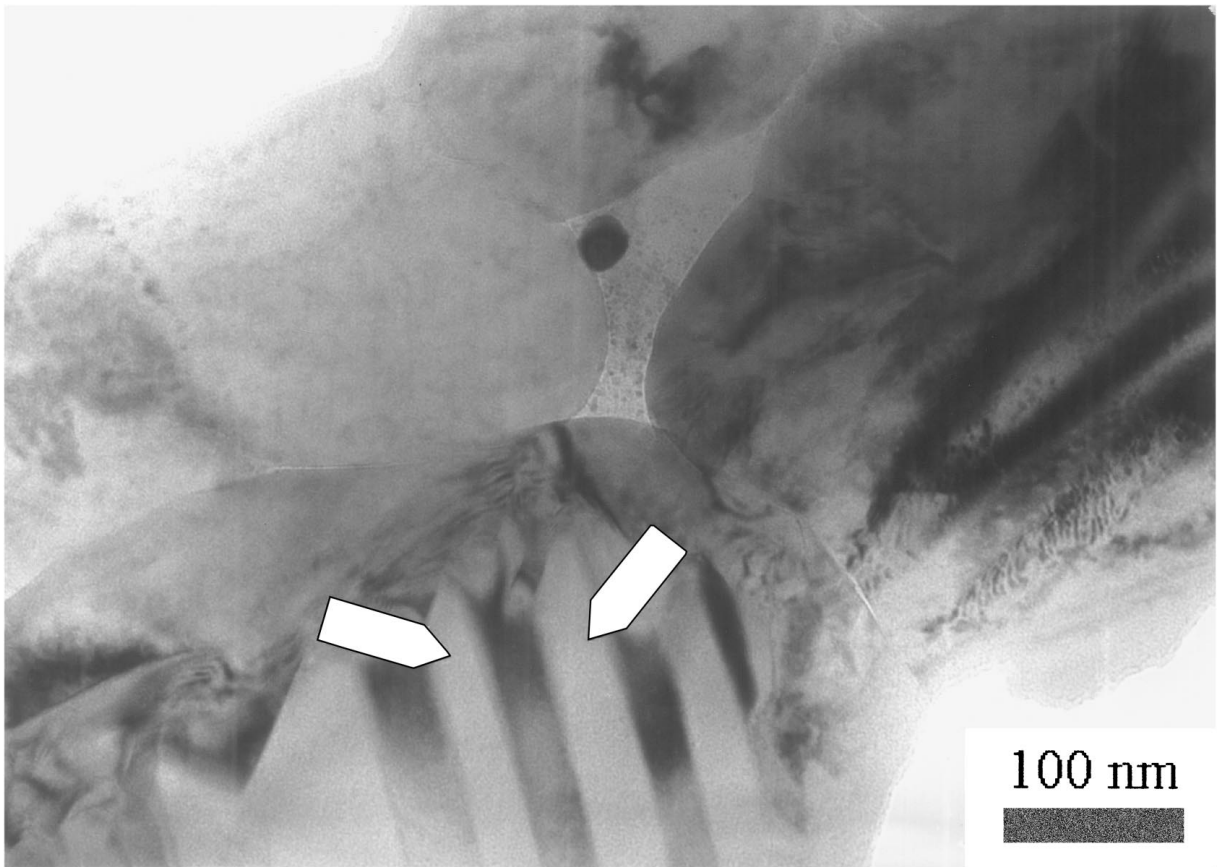
3.2. Effects of annealing in a reducing atmosphere

A cyclic thermal analysis of the glassy phase SiO_2-Al_2O_3-Y_2O_3 doped with 25 wt % CuO has been carried out in forming gas atmosphere at 1200 °C for 30 min. The annealing conditions were chosen similar to the conditions used for annealed CuO-doped-zirconia ceramic samples. Upon successive heat treatment, the typical peaks (T_g, crystallization and melting) all shift towards higher temperature until it is comparable to the spectra of an undoped SiO_2-Al_2O_3-Y_2O_3 glassy phase (the reference sample) (Fig. 7). XPS and XRD analysis of the annealed glassy phase SiO_2-Al_2O_3-Y_2O_3 doped with 25 wt % CuO reveals the presence of metallic copper.

Sintered CuO-doped-zirconia were annealed in a reducing atmosphere (forming gas) at 1200 °C for 30 min. These samples and an undoped sintered zirconia ceramic (in air at 1500 °C for 1 h) that serves as a reference, were characterized by Raman spectroscopy. Because of reasons cited in the above discussion, 0.45 wt % CuO doped zirconia sintered at 1350 °C for 1 h in air and the same sample subsequently annealed at 1200 °C for 30 min in N_2/H_2 were chosen for this study to localize CuO in the ceramic microstructure. As expected the Raman spectra of undoped zirconia is typical for a crystalline tetragonal phase (Fig. 8) as has also been observed in the X-ray diffraction spectra in the preceding section. The sintered CuO-doped-
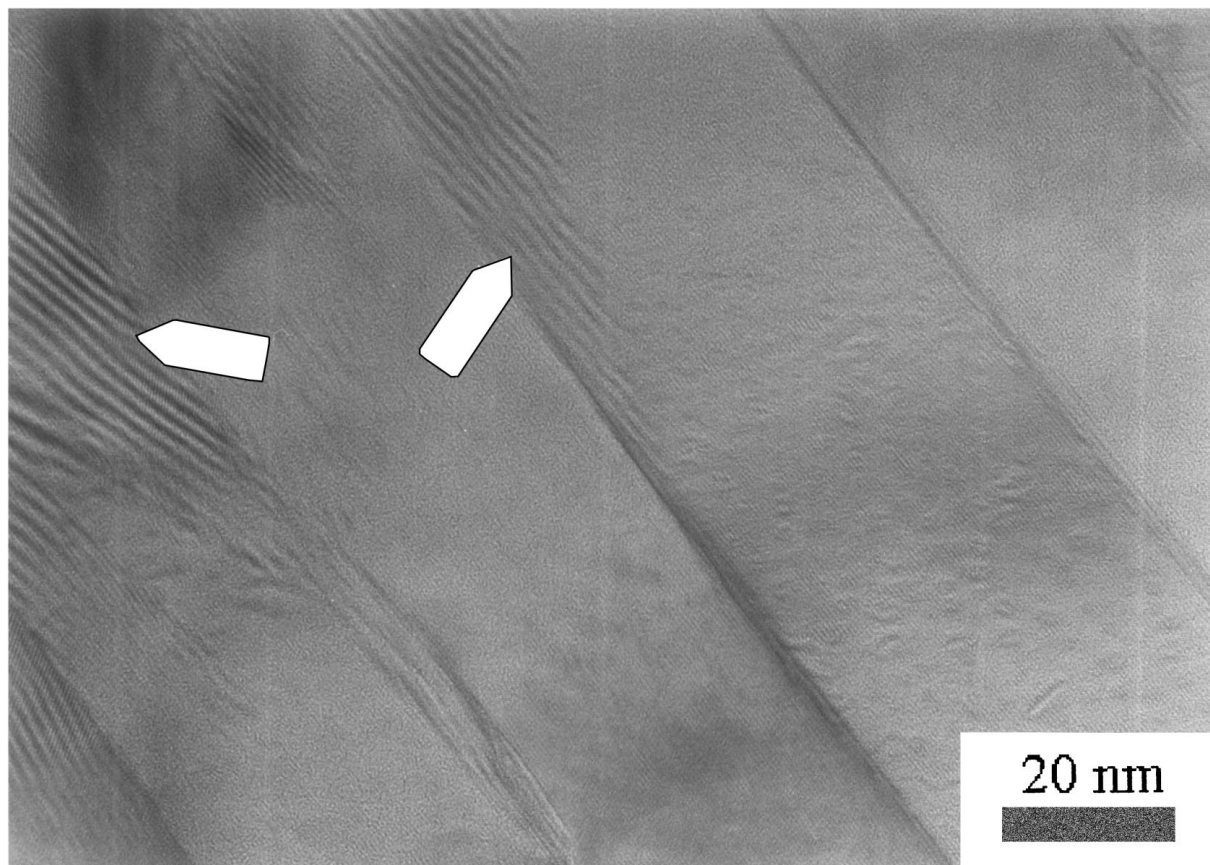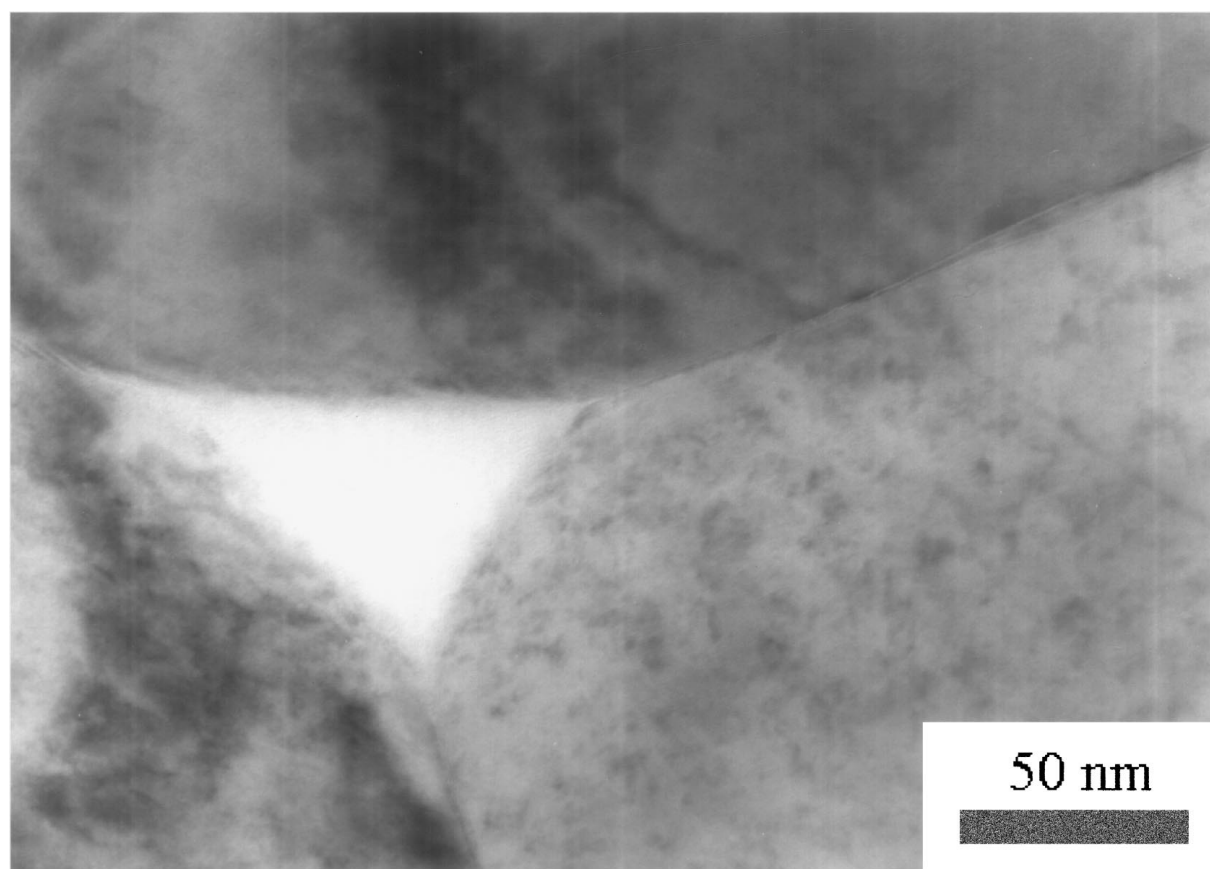
(a)

(b)

Figure 6 Transmission Electron Micrographs of CuO-doped-zirconia. (a) Typical microstructure. (b) Twins in a grain due to the typical martensitic transformation T → M. (c) Typical triple point in a zirconia doped with 0.45 wt % CuO.
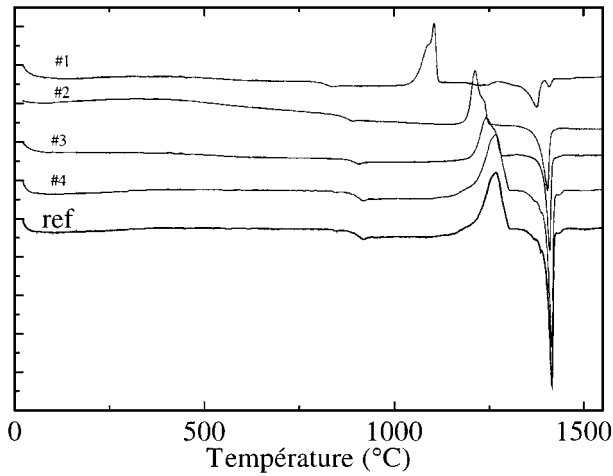
(c)

(d)

Figure 6 (*Continued*).

Figure 7 Cyclic thermal analysis of the glassy phase SiO_2-Al_2O_3-Y_2O_3 doped with 25 wt % CuO in a reducing atmosphere (ref = 0 wt % CuO).

Figure 8 Typical Raman spectra of a sintered undoped 3Y-TZP (reference).
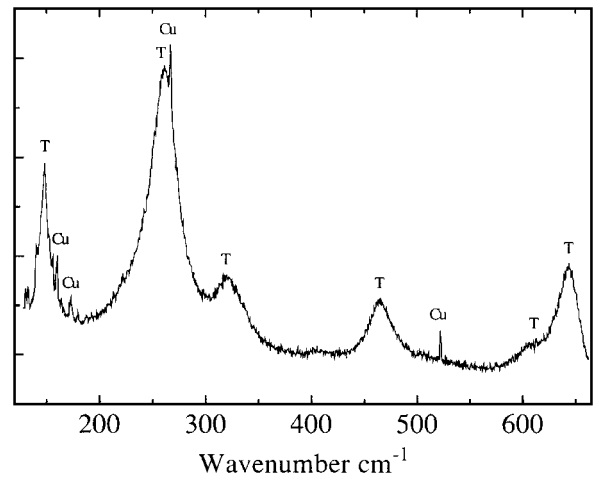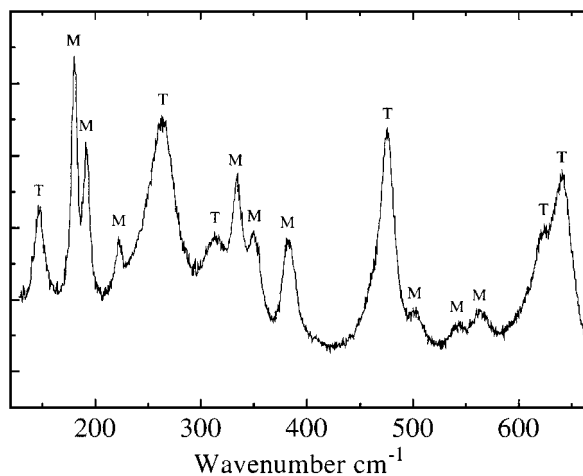

Figure 9 Typical Raman spectra of a sintered CuO-doped-zirconia.

Figure 10 Typical Raman spectra of CuO-doped-zirconia annealed in a reducing atmosphere showing interesting features attributed to metallic copper.
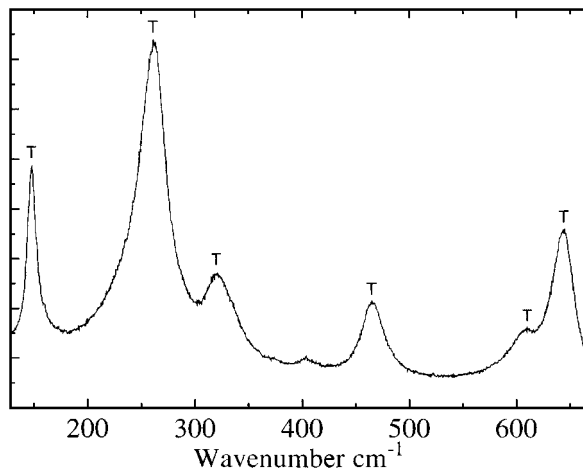
zirconia shows tetragonal phases as well as some peaks characteristic of monoclinic zirconia (Fig. 9), which are in excellent agreement with the results obtained from the X-ray diffraction. However, CuO cannot be observed in the X-ray diffraction spectra. Since Raman spectroscopy is more sensitive to the vibrational modes, we had hoped to observe traces of CuO in the zirco-

nia matrix. The characteristic feature of CuO in Raman spectra ($\sim$220 cm^{-1}) is however masked by the strong broad peak from the tetragonal phase of zirconia which is centered around 265 cm^{-1}. The annealed CuO-doped-zirconia shows similar spectra as we observe for the undoped sample with some additional interesting features observed at 160, 270 and 520 cm^{-1} attributed to metallic copper (Fig. 10). The fact that no monoclinic phase is detected after annealing of these CuO doped samples is interesting.

Transmission Electron Microscopy was carried out on an annealed CuO-doped-zirconia with 0.45 wt % CuO. The only observable difference between the microstructure of sintered CuO-doped-zirconia before and after annealing treatments is the presence of spherical particles, with a typical size of a few nanometers in the grain boundaries and in the grains (Fig. 11). HRTEM and chemical analysis of these nanoparticles would be able to throw more light on the nature of these nanoparticles, which in all probability are metallic copper as suggested from the Raman data. Also in the annealing of the glassy phase metallic copper was produced. The formation of metallic nanoparticles in a glassy phase during a heat treatment in a reducing atmosphere is well known. Numerous studies have been carried out on metal inclusions in glass especially for non linear optical applications [14]. During this annealing treatment, which is often carried out in presence of a reducing agent and/or in a reducing atmosphere, the metallic ions migrate and precipitate as metallic clusters or nanoparticles [15, 16]. The metallic nanoparticles in the zirconia grains are due to the migration of grain boundaries during the annealing treatment. Intergranular particles become intragranular.

In the present case, during the annealing treatment, the dissociation of $Y_2Cu_2O_5$ in the grain boundaries and in the triple points may lead to the formation of ionic copper which could then agglomerate into clusters leading to the formation of metallic copper nanoparticles. This would lead to an excess of yttria in the grain boundaries resulting in the migration of yttria into the zirconia grains. Upon reaching a critical concentrations, this
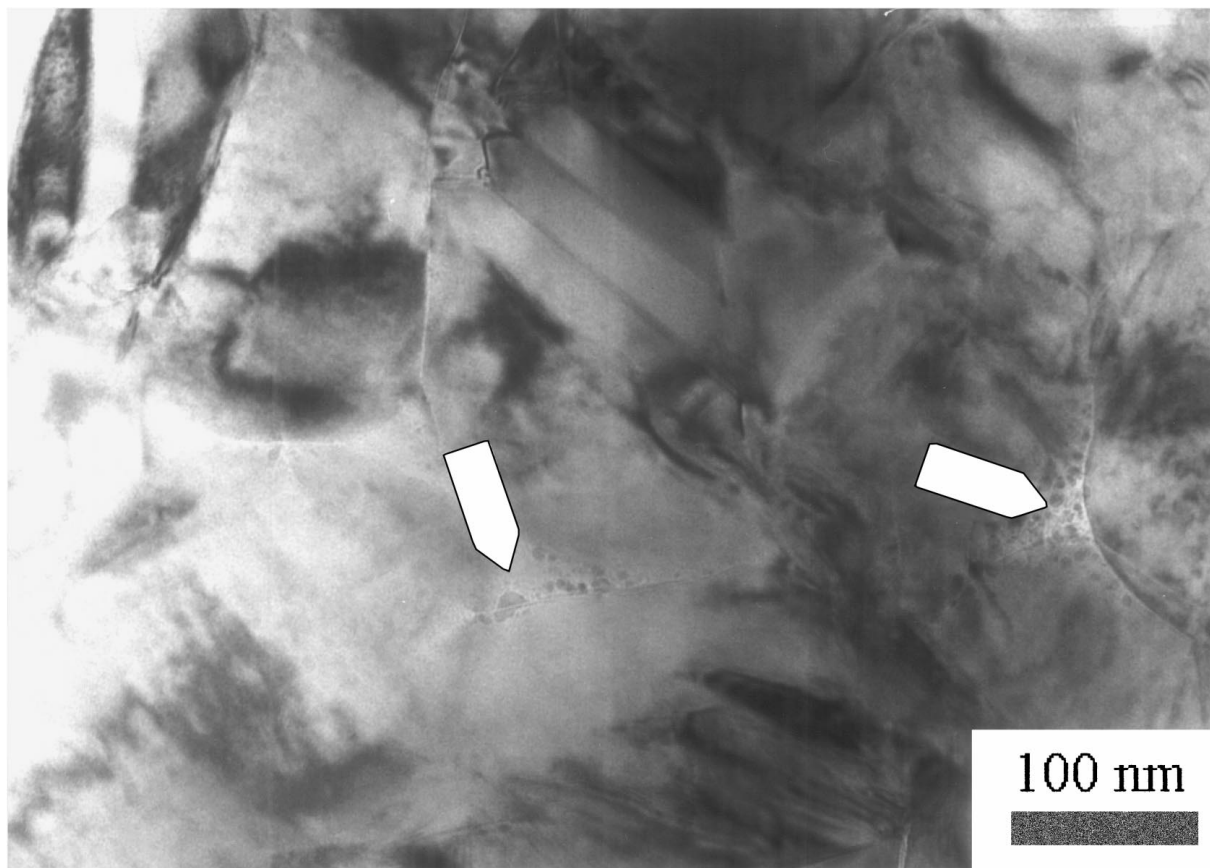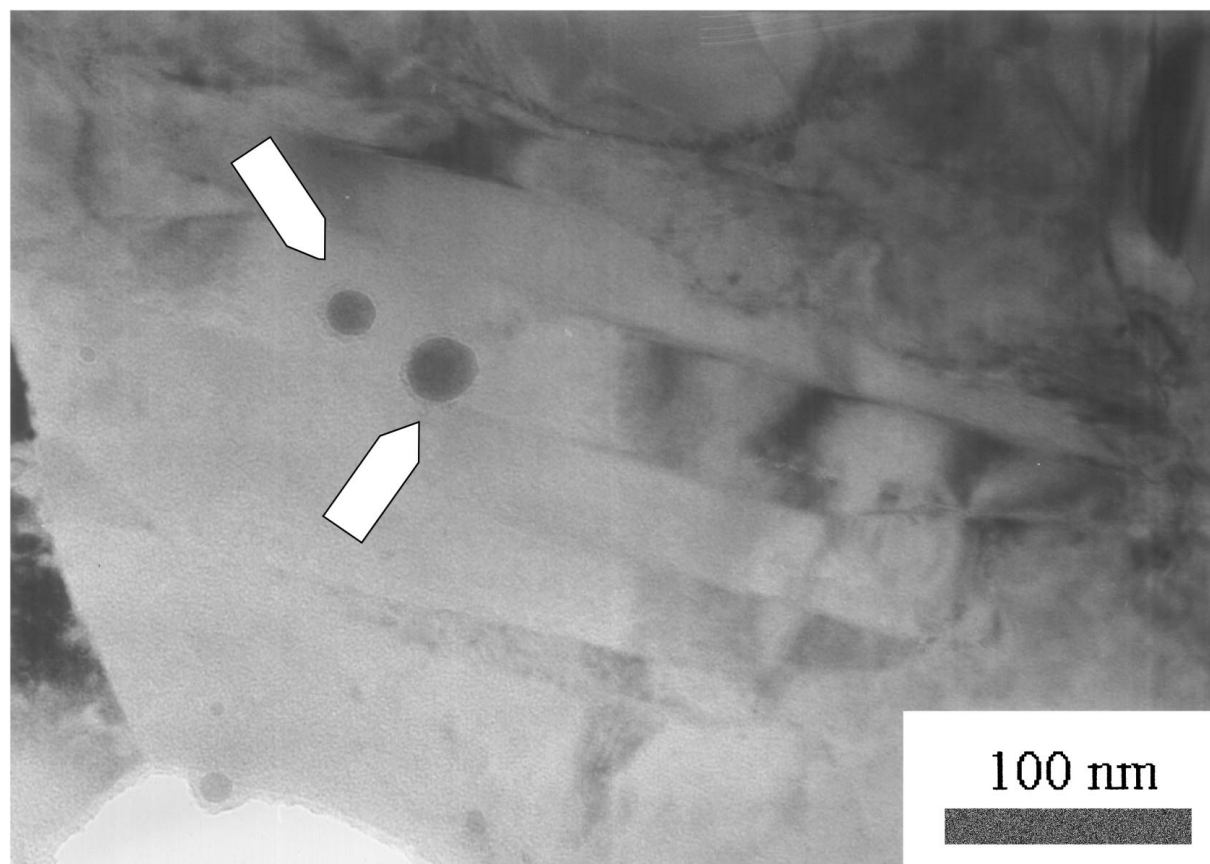
Figure 11 Transmission Electron Micrograph of CuO-doped-zirconia annealed in a reducing atmosphere. (a) Typical microstructure of zirconia doped with 0.45 wt % CuO showing the presence of particles in the grain boundaries and in the triple point. (b) Detail of a zirconia grain showing the inclusion of spherical particles. (c) Detail of a triple point with the presence of a spherical particle.
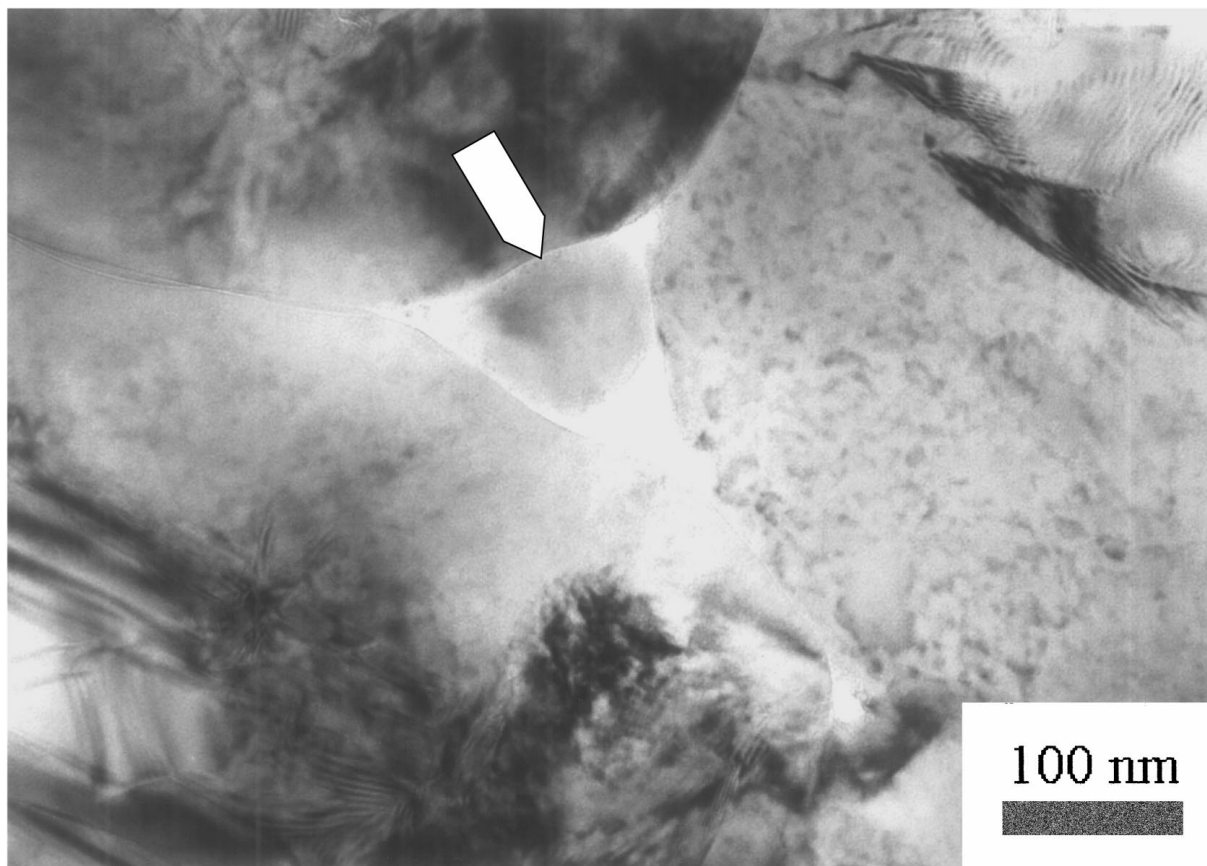
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Figure 11 (*Continued*).

(c)

would influence the monoclinic to tetragonal transition and would explain the disappearance of the monoclinic features in the Raman spectra after the annealing treatment.

4. Conclusion

DTA analysis of the sintering additives SiO_2-Al_2O_3-Y_2O_3 and CuO have shown that during the heat treatment in air, the sintering additive transforms into complex glassy phases, and crystalline $Y_2Cu_2O_5$ is observed on cooling. We have studied the influence of the percentage of CuO on SiO_2-Al_2O_3-Y_2O_3 during the heat treatment in air. With increasing CuO concentrations, the typical DTA peaks (T_g, crystallization, melting) of the sintering additive shift towards lower temperatures. During an annealing treatment in a reducing atmosphere, the dissociation of the complex glassy phases, especially $Y_2Cu_2O_5$, occur and the typical DTA peaks of the sintering additive shift towards higher temperature until they are comparable to those of an undoped SiO_2-Al_2O_3-Y_2O_3 glassy phase (the reference sample) (Fig. 11). XPS and XRD analysis of the annealed sintering additive reveal the presence of metallic copper embedded in a glassy phase matrix.

XPS analysis on sintered CuO-doped-zirconia shows that copper is not dissolved in the zirconia grains but is present in the grain boundary region and reacts with the grain boundary glassy phase consisting of SiO_2-Al_2O_3-Y_2O_3. XRD analysis on CuO-doped-zirconia with various percentages of CuO reveal that the concentration of CuO influences the transformation of the zirconia from the tetragonal to the monoclinic form. From observations made with the model system SiO_2-Al_2O_3-Y_2O_3 and CuO, we propose that it is the formation of the phase $Y_2Cu_2O_5$ in the grain boundaries and the triple points which is responsible for the change of crystalline structure by depleting the Y_2O_3 concentration in certain grains.

During annealing in a reducing atmosphere a reverse process occurs. Dissociation of $Y_2Cu_2O_5$ allows the migration of Y_2O_3 in grain boundaries toward the zirconia grains. Then, the concentration of Y_2O_3 increases in the zirconia grains and the monoclinic phase is no longer observed on cooling. The dissociation of $Y_2Cu_2O_5$ in the studies on the glassy phase alone leads to the formation of metallic copper nanoparticles. For the CuO-doped-zirconia ceramics, Raman spectroscopy indicates that metallic copper is formed and TEM micrographs show that small spherical nanoparticles are present in the triple point and in the zirconia grains. HRTEM and chemical analysis of these nanoparticles would be able to confirm the nature of these nanoparticles, which in all probability are metallic copper.

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