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Synthesis, sintering and microstructure of 3Y-TZP/CuO nano-powder composites

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Abstract

Nanocrystalline 3Y-TZP and copper-oxide powders were prepared by co-precipitation of metal chlorides and copper oxalate precipitation respectively. CuO (0.8 mol%) doped 3Y-TZP powder compacts were prepared from the nanocrystalline powders. Dilatometer measurements on these compacts were performed to investigate the sintering behaviour. Microstructure investigations of the sintered compacts were conducted. It is found that additions of the copper-oxide powders in the nanocrystalline 3Y-TZP leads to an enhancement of densification, formation of monoclinic zirconia phase and significant zirconia grain growth during sintering.

Keywords: Sintering; ZrO_2; Transition metal oxides; Nanocomposites; Microstructure-final

1. Introduction

In the past two decades, zirconia-based ceramics have found a wide range of applications due to their excellent chemical and physical properties. Among this group of materials, 3 mol% yttria stabilised tetragonal zirconia polycrystals doped with CuO is drawing increasing interest. A remarkable enhancement in superplasticity of Y-ZYP ceramics was reported when CuO (<1 mol%) was added.[1–3] Tribological studies showed that an addition of 1.8 mol% of CuO significantly reduces friction of 3Y-TZP ceramics under dry sliding situations.[4,5]

A sound knowledge of the sintering behaviour is important for the fabrication of materials with the desired microstructure and properties. As shown in a previous paper, the addition of a coarse-grained CuO powder remarkably inhibits the densification of a sub-micron 3Y-TZP (TOSOH) powder compact due to the several reactions, which occur during heating.[6] A high sintering temperature (>1400 °C) is required to sinter the ceramic to full density. The reaction between molten Cu_2O and yttria at around 1180 °C results in a depletion of yttria from the zirconia grains, and consequently leads to the formation of monoclinic zirconia during cooling.

In this work, we aimed to lower the required sintering temperature for obtaining dense 0.8 mol% CuO doped 3Y-TZP ceramics, by using nanocrystalline copper-oxide and 3Y-TZP powders. The copper-oxide powders were synthesised by a copper oxalate precipitation technique, which is used for catalysts or ceramic powders fabrication.[7–10] In this work, alcohol was used as the solvent instead of water in order to reduce particle agglomeration during drying and calcination. The nanocrystalline 3Y-TZP powder was synthesised by a co-precipitation technique. Dilatometer measurements were conducted to investigate the sintering behaviour of the composite powder compacts. Since it has been shown in a previous paper that high oxygen partial pressure is favourable for densification of CuO doped 3Y-TZP,[6] all dilatometer measurements were performed in an oxygen flow. Discussion is focused on the influences of additions of copper-oxide on densification and microstructure development during sintering.

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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 based on metal chlorides, as described in detail elsewhere.[11] An aqueous solution (1.2 M in concentration, pH ∼2) containing proper amounts of Zr^{4+} and Y^{3+} ions was added with the aid of a peristaltic pump to a concentrated aqueous ammonia (pH ∼14) solution. The ammonia solution was stirred vigorously and continuously with a top-mounted turbine stirrer. The resulting wet gel was washed until 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 μm sieve, and subsequently calcined at 550 °C in stagnant air for 2 h. The composition of the 3Y-TZP powder was confirmed by an XRF (PW 1480, Philips) analysis.

A copper oxalate precipitation method was used to prepare the nanocrystalline copper-oxide powders. $Cu(NO_3)_2·3H_2O$ (Merck Chemical, Germany) and oxalic acid ($H_2C_2O_4·2H_2O$, Merck Chemical, Germany) were separately dissolved into ethanol to form an alcohol solution in a concentration of 0.5 M. The copper nitrate solution was added to the oxalic acid solution (in 5% excess) with the aid of a separation funnel. The oxalic acid was strongly stirred by a magnetic stirrer. The dropping speed of the Cu solution was controlled to be 10–15 drops/min (roughly 1–1.5 mL/min). During the addition, a light blue complex precipitate of copper oxalate was formed. After all the Cu solution was added, the suspension was stirred for an extra 30 min and then oven-dried overnight at 100 °C. After grinding and sieving the powder was calcined at either 250 or 450 °C for 5 h. Hereafter the copper-oxide powder calcined at 250 °C is denoted as CuO-250, and the powder calcined at 450 °C is denoted as CuO-450.

Appropriate amounts of 3Y-TZP and copper-oxide powders for composites of 3Y-TZP doped with 0.8 mol% CuO were mixed by wet-milling 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 mixed powder was ground slightly in a plastic mortar and sieved through a 180 μm sieve.

2.2. Dilatometer measurements

Cylindrical green compacts of the 3Y-TZP and mixed CuO/3Y-TZP powders were prepared by isostatic pressing at 400 MPa. The diameter and length of the compacts were 7–8 mm and 12–15 mm, respectively. The green densities (measured by the Achimedes technique in mercury) of the compacts were 44–46% of the theoretical density of tetragonal zirconia. The sintering behaviour of the compacts was studied using a Netzsch 402E dilatometer under an oxygen flow. For all dilatometer measurements, a three segment temperature program was applied, including heating from room temperature at 15 °C/min, holding at 1130 °C for 2 h, and cooling to room temperature at 5 °C/min. Linear shrinkage was recorded as a function of time and temperature. The density as a function of temperature was calculated from the green density and linear shrinkage data.[6]

2.3. Characterisation

X-ray diffraction (XRD, X'pert_APD, PANalytical) analysis on 3Y-TZP, copper-oxide and the mixed powders and the sintered compacts was conducted for phase identification. The crystallite diameters of powders were calculated using the Scherrer relationship. The volume fraction of the monoclinic zirconia phase was calculated using the relationship proposed by Toraya et al.[12] The relative amount of CuO, Cu_2O and Cu-metal phase in the copper-oxide powders were estimated by the relative intensity ratio of the peaks of the XRD patterns. Specific surface areas of the powders were measured by the BET (ASAP 2400, Micromeritics) technique. The particle size of the powders was calculated from the BET surface area data assuming that all the particles in the powder are spherical:

$$D = 6/S\rho \qquad (1)$$

where S is the BET surface area and ρ is the theoretical density of the material. Scanning electron microscopy (SEM-EDX, Thermo NORAN Instruments) pictures were taken from polished and thermally etched cross-sections of the samples after dilatometer measurements.

3. Results and discussion

3.1. Powder characterisation

Fig. 1 shows the XRD patterns of 3Y-TZP, CuO-450, CuO-250 and 0.8 mol% CuO-250 doped 3Y-TZP powders. BET surface areas and equivalent spherical particle diameters as calculated from BET data of all powders are listed in Table 1.

As can be seen in Fig. 1, the 3Y-TZP powder prepared by co-precipitation possesses a well-crystallised pure tetragonal structure. The particle diameter of the 3Y-TZP powder as determined by X-ray line (1 1 1) broadening technique

Table 1
BET surface area and BET equivalent particle diameter of powders

Powder	S_{BET} ($m^2\ g^{-1}$)	D_{BET}(nm)
TZ-3Y	102	10
CuO-450	2.77	360
CuO-250	20.2	50

S_{BET}: specific surface area determined by nitrogen adsorption; D_{BET}: particle size calculated on the basis of S_{BET}.

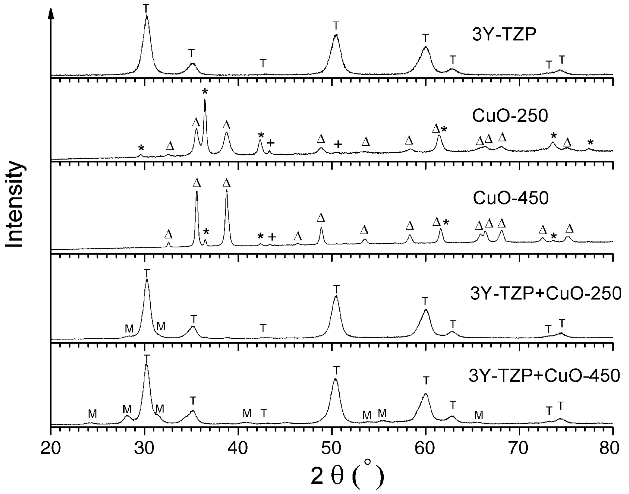

Fig. 1. XRD patterns of the as-prepared 3Y-TZP, CuO-450, CuO-250 and 3Y-TZP doped with 0.8 mol% CuO-250 powders. ((Δ) CuO peaks; (*) Cu_2O peaks; (+) Cu peaks; (T) tetragonal zirconia peaks; (M) monoclinic zirconia peaks).

and BET technique are 8 and 10 nm, respectively. This good agreement between the particle diameter data implies that the 3Y-TZP particles are weekly (or not) aggregated.

Both CuO-250 and CuO-450 powders contain three crystalline phases: CuO, Cu_2O and metallic Cu (see Fig. 1). However, the powders show a significant difference in phase distribution. As calculated from the relative X-ray intensity ratios the CuO-250 powder contains 50 vol% Cu_2O while CuO-450 contains mainly CuO (93 vol%). These results are in good agreement with the investigations on thermal decomposition of copper oxalate, which showed that copper oxalate decomposes partially into copper metal with stepwise cation reduction ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$) between 250 and 300 °C and then oxidises to CuO between 280 and 400 °C.[13,14] Additionally, the copper-oxide powders showed a strong dependence of particle/aggregate size on calcination temperatures. The primary particle diameter of CuO-250 and CuO-450 as determined by X-ray line broadening technique are 20 and 50 nm, respectively. However, both powders show considerably larger BET equivalent particle diameters (50 and 360 nm for CuO-250 and CuO-450, respectively, see Table 1) if compared with their primary particle diameters. It can be said that in those two copper-oxide powders particles are strongly aggregated, while higher calcination temperatures lead to lager crystallite sizes and even stronger aggregations of the primary particles.

The 3Y-TZP powders mixed with CuO-450 and CuO-250 showed similar XRD patterns. In both mixed powders a small portion (<15 vol%) of monoclinic zirconia phase was present, which was not detected in the original 3Y-TZP powder. This formation of monoclinic zirconia could be caused by the tensile stress introduced to the zirconia particles during the mixing. It is generally accepted that a tetragonal to monoclinic phase transformation of zirconia can result from applied tensile stresses.[15] Cu phases can hardly be detected in the XRD pattern of the mixed powders due to the low amount of copper-oxide additions (0.8 mol%).

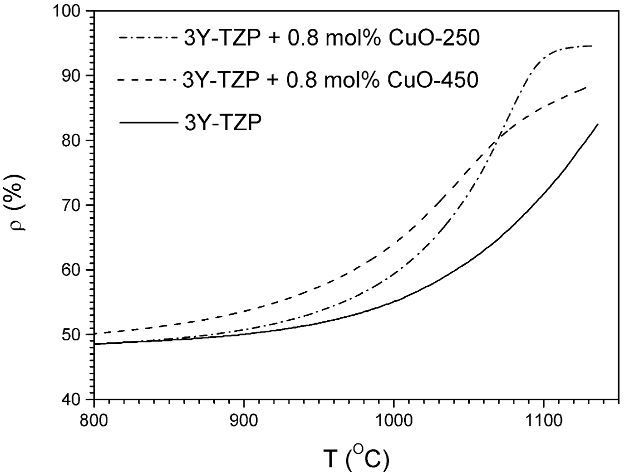

Fig. 2. Densities of 3Y-TZP and 3Y-TZP doped with 0.8 mol% CuO-250 and CuO-450 during heating.

It has to be pointed out that the number of copper oxide particles per unit volume of powder is different for CuO-250 and CuO-450 doped 3Y-TZP powders. As can be easily calculated from the aggregate sizes (360 nm of CuO-450 and 50 nm of CuO-250), the volume of a copper oxide aggregate/particle is 370 times larger for CuO-450 than for CuO-250. This means that the number of copper oxide aggregates/particles per unit powder volume for the 3Y-TZP/CuO-450 powder compact is 370 times less than for the 3Y-TZP/CuO-250 powder compact. Therefore, in the 3Y-TZP/CuO-450 powder compact 3Y-TZP particles are in much less contact with copper oxide particles when compared with the 3Y-TZP/CuO-250 powder compact.

3.2. Sintering

Sintering properties of the powder compacts were investigated using a dilatometer. Figs. 2 and 3 show the densities and linear shrinkage rate of the undoped 3Y-TZP and 3Y-TZP doped with 0.8 mol% CuO-250 and CuO-450 powder compacts during heating.[a] Generally, it can be said that the samples prepared from nanocrystalline 3Y-TZP powders show a more active sintering behaviour if compared with the samples prepared form sub-micron commercial (e.g. Tosoh) powders.[16] All samples start to densify at around 900 °C. After dilatometer experiments including the holding at 1130 °C for 2 h and cooling down to room temperature, all samples have a final density more than 94%.

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[a] All samples experienced a slight shrinkage at temperatures below 400 °C, which might be caused by the loss of adsorbed water (not shown in these figures). Therefore, the starting densities shown in Fig. 1 are a bit higher than the green densities measured before the experiments. Also, there is a small starting density difference between the samples probably due to the slight difference of compaction properties and water adsorption capability of those samples.

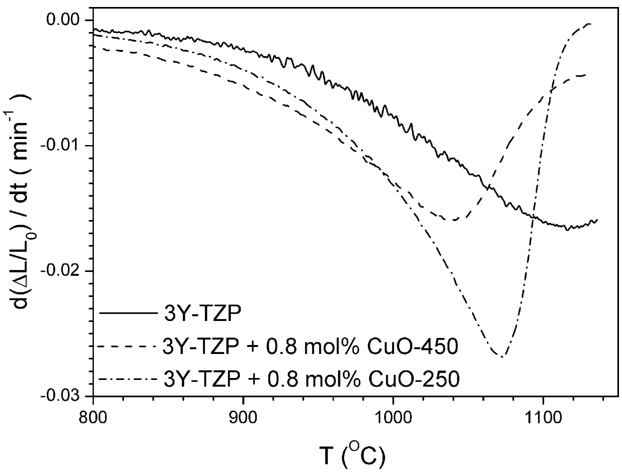

Fig. 3. Linear shrinkage rate of 3Y-TZP and 3Y-TZP doped with 0.8 mol% CuO-250 and CuO-450 during heating.

As can be seen from Figs. 2 and 3, both CuO-450 and CuO-250 additions strongly increase the densification of nanocrystalline 3Y-TZP system. However, the characteristics of the added copper-oxide powders have considerable influence on densification. Comparing the dilatometer results of the two CuO doped samples, one can see that they behave similarly in the early densification stage (800–1000 °C) but differ in the intermediate stage (1000–1100 °C). With increasing temperature the densification rate of CuO-250 doped sample increases dramatically up to 1080 °C. At that temperature a density of 85% has been reached and the densification rate starts to saturate. The sample densifies to 94% before the holding stage is reached, indicating that the sintering temperature for obtaining a dense sample can be lowered. For the CuO-450 doped sample, the maximum in densification rate appears at around 1040 °C, while the density is much lower than that of the CuO-250 doped sample at its maximum densification rate (75% compared with 85%). When the heating stage is finished, the density of the CuO-450 doped sample is only 88%. Compared with the CuO-250 doped sample, the CuO-450 doped sample experienced an inhibition of densification. One of the possible reasons for the slower densification of the CuO-450 doped sample is the larger particle/aggregate size of the copper-oxide. As discussed in a previous paper,[6] dissolution of copper-oxide in the Y-TZP matrix occurs in the early sintering stage of CuO doped 3Y-TZP (800–1000 °C), and increases ion mobility in the 3Y-TZP grains and especially in the grain boundary region. This high ion mobility or ion diffusivity results in an enhancement of sintering and consequently leads to a lower on set temperature of densification and/or high densification rate. So one can understand that the amount or size of the contact area between 3Y-TZP and copper-oxide particles in the compacts actually determines the sources of densification enhancement in this sintering stage. Compared with the CuO-250 doped sample, the CuO-450 doped sample contains much less 3Y-TZP/CuO contact area due to the larger size of CuO aggregates and consequently densifies much slower at this sintering stage.

3.3. Microstructure

Fig. 4a and d show SEM pictures of polished and thermally etched cross-sections of the undoped and 0.8 mol% CuO-250 doped 3Y-TZP after the dilatometer experiments. The CuO-450 doped sample is not suitable for SEM study because it badly cracks after sintering and the CuO distribution is extremely inhomogeneous.

As shown on these SEM images, the undoped 3Y-TZP sample can be characterised as a dense ceramic containing fine zirconia grains with a mean size of 160 nm (determined by linear intercept technique[17] on the basis of SEM images). In contrary, the CuO-250 doped sample contains evolved zirconia grains with a size up to 700 nm, indicating a significant enhancement of 3Y-TZP grain growth during sintering due to the addition of small amounts of nano-sized copper-oxide particles. Among the zirconia grains, some well-crystallised bright grains can be occasionally found in the CuO-250 doped sample (as denoted by the arrow in Fig. 4d). An EDX analysis shows that these bright grains contain much more Cu than the neighbouring grains.

SEM analysis on the CuO-250 doped samples fired at various temperatures (with a heating rate of 15 °C/min) was conducted for investigation of grain growth during heating. It was found that the grains grew from 10 nm to 50 nm during the heating from room temperature to 900 °C. With further heating to 1000 ° C, the grains grew rapidly to 100 nm. For undoped 3Y-TZP compacts, made from the same type of powders the grain sizes of 20 nm, 30 nm and less than 40 nm were observed after sintering at respective 900, 1000 and 1050 °C.[18] From these results it can be concluded that an enhancement of zirconia grain growth in the CuO-doped 3Y-TZP system has started in the intermediate sintering stage, while this is not the case for pure undoped 3Y-TZP. As stated in the discussion above, at around 900 °C the partial dissolution of CuO in 3Y-TZP matrix increases the ion diffusivity in the 3Y-TZP grains and/the grain boundary region. It seems that the enhanced zirconia grain growth is also caused by this increase in ion diffusivity as a result from the CuO dissolution.

Phase composition of the undoped, CuO-450 and CuO-250 doped 3Y-TZP samples after dilatometer measurement were determined by XRD analysis (Fig. 5). Whereas the undoped 3Y-TZP sample showed a pure tetragonal zirconia structure, the CuO-doped samples contain significant amounts of a monoclinic zirconia phase (60 and 70 vol% for CuO-450 and CuO-250 doped samples respectively).

Since the crystallite structure of dense pure (non CuO-doped) 3Y-TZP ceramics with a grain size of 700 nm should be almost 100% tetragonal,[19] it seems that the presence of CuO in the composites influences the stability of the tetragonal phase. Many studies on CuO doped 3Y-TZP system showed the formation of monoclinic zirconia during sinter-

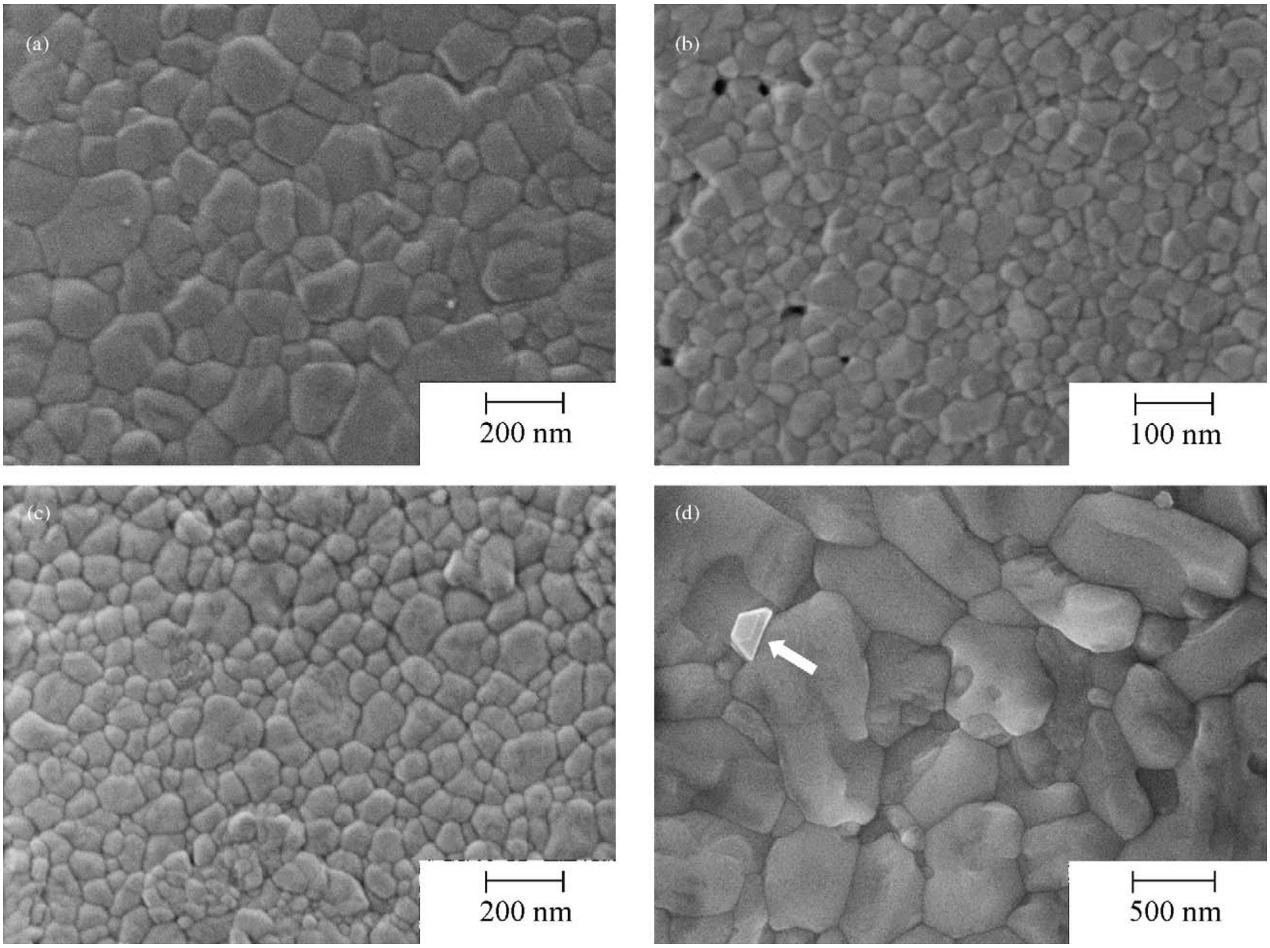

Fig. 4. SEM of cross-sections of sintered undoped and 0.8 mol% CuO-250 doped 3Y-TZP. (a) 3Y-TZP sintered at 1150 °C for 2 h. (b) 3Y-TZP doped with 0.8 mol% CuO-250 sintered at 900 °C for 30 min. (c) 3Y-TZP doped with 0.8 mol% CuO-250 sintered at 1000 °C for 30 min. (d) 3Y-TZP doped with 0.8 mol% CuO-250 sintered at 1130 °C for 2 h.

ing, which was explained by the depletion of yttrium in the zirconia grains due to the solid–liquid reaction between CuO and yttria at around 1180 °C.[20,21] In the case treated in this paper, the sintering temperature (1130 °C) is below the Y-TZP/CuO liquid/solid reaction temperature (1180 °C). The formation of monoclinic zirconia phase in our case requires further investigations.

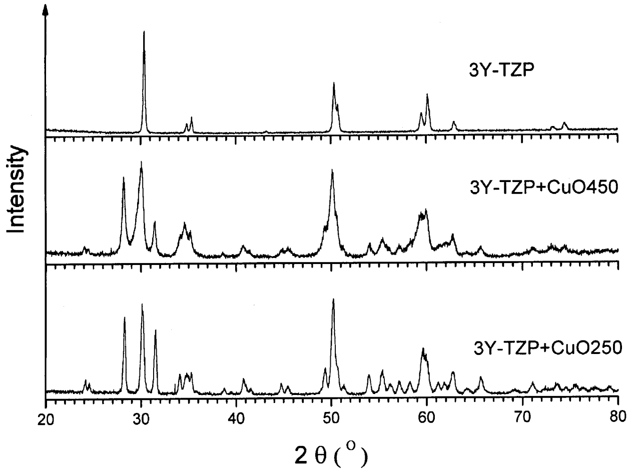

Fig. 5. XRD patterns of undoped and 0.8 mol% CuO-450 and CuO-250 doped 3Y-TZP after dilatometer measurements.

4. Conclusions

Nano-crystalline powders of 3 mol% yttria stabilised zirconia and copper-oxide were successfully prepared by co-precipitation and copper oxalate precipitation respectively. The 3Y-TZP powder consists of weakly agglomerated, pure tetragonal zirconia particles containing small aggregates with an average diameter around 10 nm. The particle/aggregate size of copper-oxide powder strongly depends on calcination temperature.

The 3Y-TZP/CuO composites prepared from nanocrystalline powders show very high sintering activities. All the samples investigated in this work can be densified to 94% by sintering at 1130 °C for 2 h. Addition of nanocrystalline copper-oxide further increases the densification of nanocrystalline 3Y-YZP system and leads to a tetragonal to monoclinic phase transformation of zirconia grains during sintering. The

3Y-TZP doped with CuO-450 (450 °C calcined copper-oxide, with a BET particle size of 360 nm) sinters less effectively when compared with the CuO-250 (250 °C calcined copper-oxide, with a BET particle size of 50 nm) doped one. The addition of CuO-250 in 3Y-TZP results in strong enhancement of grain growth of zirconia during sintering.

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