

The effect of copper oxide on sintering, microstructure, mechanical properties and hydrothermal ageing of coated 2.5Y-TZP ceramics

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Copper oxide dopants in amounts up to 1 wt% were added to 2.5 mol% yttria-coated zirconia powders in studies of sintering, microstructure, mechanical properties and hydrothermal ageing behaviour. High densities ($>6 \text{ Mgm}^{-3}$), high tetragonal phase content ($>95\%$), and phenomenal fracture toughness values ($>17 \text{ MPam}^{1/2}$), were obtained for lower dopant levels. Grain sizes of 0.13 to 0.25 μm were measured for all samples sintered at 1300 °C. Rounded pores in some doped samples indicated that a liquid phase was involved during sintering. Copper oxide additions aid low temperature sintering and offer potential for property enhancement with a particularly high toughness being measured as well as improving resistance to structural degradation in 180 °C hydrothermal ageing.

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1. Introduction

Zirconia-based materials offer performance advantages by alleviating many of the problems associated with other engineering ceramics. The properties of 2.5 mol% yttria-stabilised zirconia include fracture toughnesses of greater than 12 $\text{MPam}^{1/2}$ and tensile strengths of 1000–1500 MPa [1, 2]. In addition zirconia-based ceramics possess good ionic conductivity [3]. Typically, stabilised zirconias are being utilised for adiabatic diesel engine parts, as thermal barrier coatings, oxygen sensors, fuel cells, heating elements, polymer processing dies, extrusion dies, grinding media, bioceramics components, cutting tools, scissors and knives.

In order to utilise these materials for engineering applications, the avoidance of undesirable phase transformations and the retention to room temperature of high amounts of the desirable tetragonal phase are necessary. These are achieved by doping zirconia with yttria to produce high density tetragonal zirconia polycrystalline ceramics known as Y-TZP.

Y-TZP ceramics possess high fracture toughnesses as a result of the tetragonal (t) to monoclinic (m) phase transformation which occurs in the vicinity of a crack tip, the mechanism known as transformation toughening. However, the effectiveness of this mechanism is dependent on the processing history of the starting powders (e.g. methods of yttria incorporation either by a coating or co-precipitation technique) which has a significant influence on the sintered microstructure

and mechanical properties of the resulting body. It was shown in previous work [4, 5], that 2.5 mol% Y-TZP materials consisting of small tetragonal grains and made from a coated powder exhibited high fracture toughness (K_{Ic}) which was attributed mainly to the inhomogeneous distribution of yttria in the tetragonal grains resulting in enhanced transformability of the grain core, (e.g. average grain sizes of 0.24 and 1.08 μm gave fracture toughness values of 12.2 and 6.7 $\text{MPam}^{1/2}$ respectively). On the other hand the fracture toughness of equivalent co-precipitated ceramics increased with increasing grain size (e.g. for grains of 0.38 and 0.98 μm fracture toughnesses of 5 and 10.2 $\text{MPam}^{1/2}$, respectively were measured).

One of the major limitations of Y-TZP ceramics as engineering materials is the undesirable surface-initiated tetragonal to monoclinic phase transformation, accompanied by property degradation during exposure to low temperature water or aqueous solutions [6]. The underlying mechanism is still under debate but it is generally understood to be associated with hydroxyl ion incorporation in the zirconia lattice and the destabilisation of the tetragonal grains.

The inclusion of additives which form liquids in Y-TZP powders during sintering, in particular of transition metal oxides [2, 7, 8] is likely to affect hydrothermal ageing resistance if they aid sintering at relatively low temperatures (i.e. $\leq 1300 \text{ °C}$) and result in densification without grain growth. In addition, these additives have been shown to enhance superplasticity in Y-TZP

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[9] and other ceramics [10] behaviour which is believed to be associated with the formation of a low viscosity grain boundary film.

The aim of this present work was to identify the optimum amount of copper oxide (CuO) addition to coated 2.5Y-TZP powders. Evaluation of the materials involved sintering studies conducted at a range of temperatures, with compositions assessed in terms of tetragonal phase retention, densification, grain sizes, fracture toughness and hardness. The tetragonal phase stability in hydrothermal conditions was also studied.

2. Experimental procedure

2.1. Sample preparation

Commercially available 2.5 mol % yttria-stabilised zirconia (2.5Y-TZP) powders were prepared [11] and supplied by Tioxide Specialties Ltd., UK. The as-received 2.5Y-TZP powder had a total impurity concentration of about 1.7 wt %, with 0.08 wt % Al_2O_3 and 1.6 wt % HfO_2 as the major impurities. Varying amounts of CuO (0.05, 0.1, 0.2, 0.5 and 1 wt %) were incorporated into the Y-TZP in an attritor-mill [8].

Disc samples (19 mm diameter and weighing ~ 3 g) were made by uniaxial pressing at 35 MPa followed by cold isostatic pressing at 200 MPa. The sintering behaviour of the doped materials was investigated over the temperature range 1250 to 1500 °C at a furnace ramp rate of 10 °C/min. and for holding times of 2 h. All sintered samples were polished on one face to a 1 μm surface finish prior to testing.

2.2. Characterisation

The specific surface areas of all the powders were determined using the single point BET method (nitrogen absorption and desorption) on a Micromeritics Flowsorb II 2300 and Desorb 2300A instrument. The bulk densities of the sintered samples were measured by a water immersion method. Phase analysis by X-ray diffraction of polished samples was carried out at room temperature. The fraction of surface monoclinic content was evaluated using the method of Toraya *et al.* [12]. Fracture toughness (K_{Ic}) and microhardness (H_v) were measured on polished samples using the Vicker's indentation method at loads of up to 588 N. The K_{Ic} values were computed according to the equation derived by Niihara *et al.* [13]:

$$K_{Ic} = 0.035(a/\ell)^{1/2}(E\Phi/H_v)^{2/5}(H_v/\Phi)a^{1/2} \quad (1)$$

where ℓ is the average crack length, E the Young's Modulus, H_v the Vicker's hardness, a the indent half diagonal and Φ the constraint factor (determined empirically as ~ 3 [14]).

The hardness was obtained using the standard equation for Vickers geometry:

$$H_v = 0.4635P/a^2 \quad (2)$$

where P is the indentation load. Six measurements were made for each sample and average values were obtained. In addition, microstructural evolution was examined by scanning electron microscopy (SEM). The

TABLE I The compositions and characteristics of the starting powders

Yttria content (mol %)	2.5	2.5	2.5	2.5	2.5	2.5
CuO addition (wt %)	0	0.05	0.1	0.2	0.5	1
Average specific surface area (m^2/g)	14.62	14.82	14.47	14.33	14.00	12.23
% Monoclinic content	94.48	98.72	98.71	98.10	98.35	99.09

grain size was determined on thermally etched specimens from scanning electron micrographs using the line intercept analysis of Mendelson [15]. Hydrothermal ageing at 180 °C was conducted in steam in an autoclave at 1 MPa pressure for up to 200 h. Phase stability and bulk density changes were monitored.

3. Results and discussion

3.1. General characteristics

The physical properties of the resulting powders, used in the work being reported, are presented in Table I. Specific surface areas were at a maximum of 14.82 m^2/g for 0.05 wt % CuO dopant but only for the 1 wt % material was there really a significant change, down to 12.23 m^2/g .

3.2. Tetragonal phase retention

The effects of sintering temperature on the tetragonal phase retention of the undoped and CuO-doped Y-TZP samples are shown in Fig. 1. The graph distinctively shows that the additions of CuO (up to 0.2 wt %) to these Y-TZP ceramics were beneficial in aiding the retention of high tetragonal phase ($>95\%$) when sintered at relatively low temperatures (i.e. 1250 °C) if compared to the undoped Y-TZP which only attained $\sim 41\%$ tetragonal content for 1250 °C sintering.

The low tetragonal content in the low temperature sintered body of the undoped ceramic can be attributed to the fact that since the yttria distribution in the starting powder was inhomogeneous, the ZrO_2 grains would not have achieved a sufficiently uniform yttria content to stabilise the tetragonal phase to room temperature. However, as the sintering temperature was increased by 50 °C, as shown in Fig. 1, the undoped ceramic showed a sharp increase in the retention of tetragonal phase (i.e. from $\sim 41\%$ at 1250 °C to $\sim 97\%$ at 1300 °C) which is in good agreement with previous work on this material [4, 5].

Higher sintering temperatures and the increased yttria diffusion rates would have allowed greater tetragonal phase stability to room temperature. However, it has been shown that even for these higher sintering temperatures an intragranular Y_2O_3 concentration gradient exists in yttria-coated zirconia ceramics [4, 16, 17].

In general, the additions of CuO were observed to be either beneficial or detrimental to the tetragonal phase stability of these coated 2.5Y-TZP specimens. The additions of CuO up to 0.2 wt % promoted higher tetragonal phase stability at room temperature than shown by the undoped ceramics throughout the sintering regime employed. In contrast, the additions of CuO above 0.2 wt % had a detrimental effect on the tetragonal phase stability

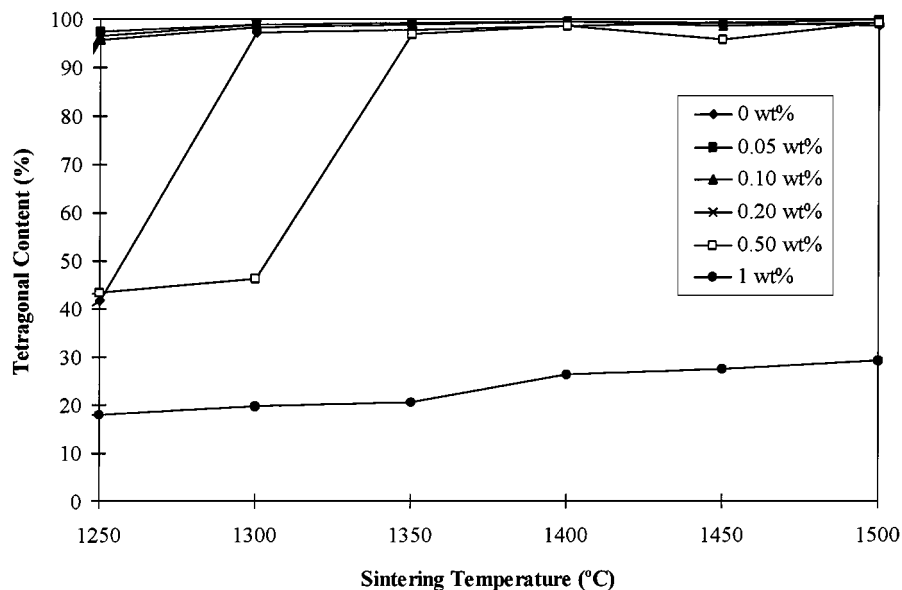


Figure 1 The effects of sintering temperature on the tetragonal phase retention of undoped and CuO-doped Y-TZPs.

if compared to the undoped ceramics. The 0.5 wt% CuO addition sample did not show significant improvement in the stabilisation of tetragonal phase to room temperature if compared to the undoped ceramic and required a higher sintering temperature (i.e. 1350 °C) before it could attain above 96% tetragonal content. The samples containing 1 wt% CuO could not be sintered to retain an acceptable amount of tetragonal phase in the zirconia structure throughout the sintering regime employed, see Fig. 1. In addition, all of the 1 wt% CuO-doped samples cracked on cooling from the sintering temperature due mainly to the high monoclinic phase.

Although the method of incorporating yttria into the zirconia is referred to as 'coating', the pre-sintered powders were monoclinic containing localised yttria concentrations. For copper oxide contents of 0.05–0.2 wt%, high tetragonal phase retention was due to smaller grains from improved sinterability at lower temperatures and to some yttria re-distribution from its dis-

solution in a copper-rich liquid phase formed during sintering. According to Mecartney [18] and Gust *et al.* [19] greater amounts of grain boundary liquid phase, such as would develop from higher CuO contents, are incorporated at triple grain boundary junctions rather than distributed along grain edges. Therefore the effect of this for the 1 wt% CuO addition samples in the present work would have been for more yttria dissolution without improved re-distribution and tetragonal phase destabilisation would have resulted.

3.3. Bulk density measurement

The bulk density variations with sintering temperatures for the CuO-doped and undoped Y-TZPs are shown in Fig. 2. The samples with 0.05, 0.10 and 0.2 wt% copper oxide exhibited similar densification behaviour, (i.e. bulk density increased for up to 0.05 wt% CuO additions then remained almost constant for CuO contents up to 0.2 wt%). For the undoped samples and those

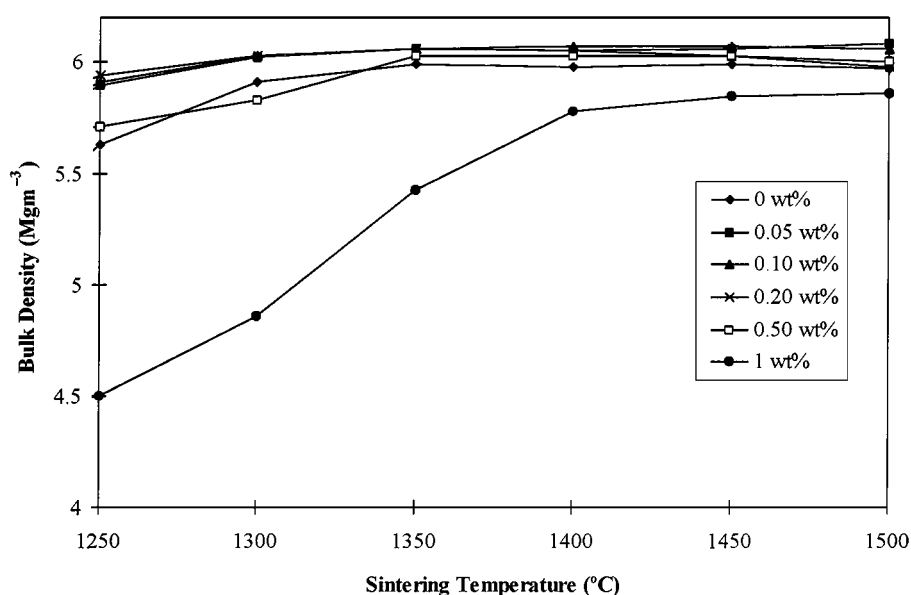


Figure 2 The effects of CuO contents and sintering temperature on the bulk density of coated 2.5Y-TZP ceramics.

with higher CuO contents there were decreased bulk densities, see Fig. 2. Sintering at 1250 °C gave low values, (i.e. from 4.5 to 5.94 Mgm⁻³ for 1 and 0.2 wt % copper oxide doping respectively), which could have been due to a combined effect of the development of monoclinic phase in the structure and the presence of residual pores.

As the sintering temperature was increased beyond 1250 °C, there was a significant increase in density for all compositions. The 1 wt % CuO-doped samples exhibited an almost constant density of ~5.85 Mgm⁻³ only after 1400 °C sintering. The measured densities of the CuO-doped (up to 0.5 wt %) ceramics when sintered above 1300 °C were generally all above 6 Mgm⁻³, higher than values exhibited by the undoped Y-TZP. On the other hand, the 1 wt % CuO doping was detrimental and samples exhibited low bulk densities throughout the sintering regime employed as compared to the undoped ceramics.

The lower densities of the 1 wt % CuO-doped materials resulted from high porosity and high monoclinic content. This significant amount of porosity is believed to have developed from the dissociation of CuO at ~1026–1031 °C, to produce Cu₂O and oxygen. At higher sintering temperatures oxygen could escape from the lower viscosity copper oxide-based liquid, thus allowing the increased densification shown in Fig. 2. The 5.85 Mgm⁻³ density measured for the 1500 °C sintering sample containing 1 wt % CuO dopant is concomitant with the high monoclinic content of the sintered body.

3.4. Fracture toughness & hardness measurement

The fracture toughnesses of all compositions except for the highest CuO additions exhibited very similar trends as the sintering temperature increased, Fig. 3. It should be mentioned here that this trend of increasing K_{IC} with

decrease in grain sizes from low temperature sintering is only observed for coated Y-TZP ceramics [4, 5, 8] and is attributed to an inhomogeneous stabiliser distribution resulting in yttria enrichment at the rim of the grain giving a core—shell structure [4, 16, 17]. Normally the centres of the grains are tetragonal but with little stabiliser present, in extreme cases the centres are monoclinic. This is clearly beneficial as the majority of the grains with low yttria content is highly metastable leading to enhanced fracture toughness through transformation toughening.

However, during sintering at higher temperatures grain growth occurs with a concomitant increase in the fraction of cubic phase which contained in excess of 8 mol % yttria and at the same time a reduction in yttria gradients across the tetragonal grains would have been expected in this coated Y-TZP i.e. the stabiliser becoming more homogeneously distributed. As a result, the tetragonal grains started to lose their metastable nature, i.e. became more difficult to transform, with a reduced transformation toughening effect [8], see Fig. 4. Greater cubic contents would also have reduced transformability under stress.

In the present work additions of small amounts of CuO (up to 0.2 wt %) could have caused redistribution of yttria to occur thereby reducing the concentration of the stabiliser in the shell of the ZrO₂ grains relative to that in the undoped material. The overall yttria content in the grains would have decreased as some yttria would have been taken into solution with the Cu-rich liquid, the amount remaining not being below some critical level required for stabilisation to occur.

Therefore, this small overall reduction in stabiliser contents in the low CuO-doped material would certainly have enhanced the transformability of the grains, i.e. increasing the transformation toughening effect. This theory was supported by the high fracture toughness values calculated using Niihara's equation and shown in Fig. 3.

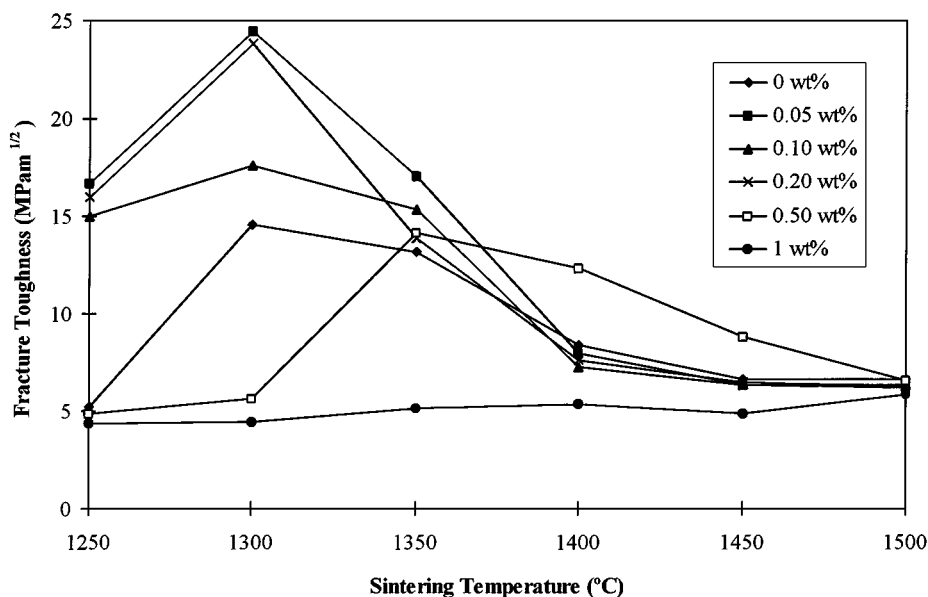


Figure 3 The effects of sintering temperature on the average fracture toughness of undoped and CuO-doped coated 2.5Y-TZP ceramics according to Niihara's equation. (Indentation load = 490 N).

TABLE II Maximum measured K_{Ic} values ($\text{MPa m}^{1/2}$) at room temperature of undoped and CuO-doped Y-TZPs

Compositions	K_{Ic} based on Palmqvist crack according to			Sintering temperature ($^{\circ}\text{C}$)
	Equation 1 [20]	Equation 3 [21]	Equation 4 [22]	
0.05 wt % CuO	24.45 ± 5.22	29.57 ± 6.31	19.20 ± 0.99	1300
0.2 wt % CuO	23.78 ± 8.27	28.96 ± 9.98	18.76 ± 1.38	1300
0.1 wt % CuO	17.64 ± 1.15	21.35 ± 1.38	17.21 ± 0.56	1300
Undoped	14.61 ± 0.56	17.10 ± 0.76	15.46 ± 0.37	1300
0.5 wt % CuO	14.16 ± 0.47	17.40 ± 0.58	15.18 ± 0.36	1350
1 wt % CuO	5.82 ± 0.91	6.77 ± 1.06	5.09 ± 1.46	1500

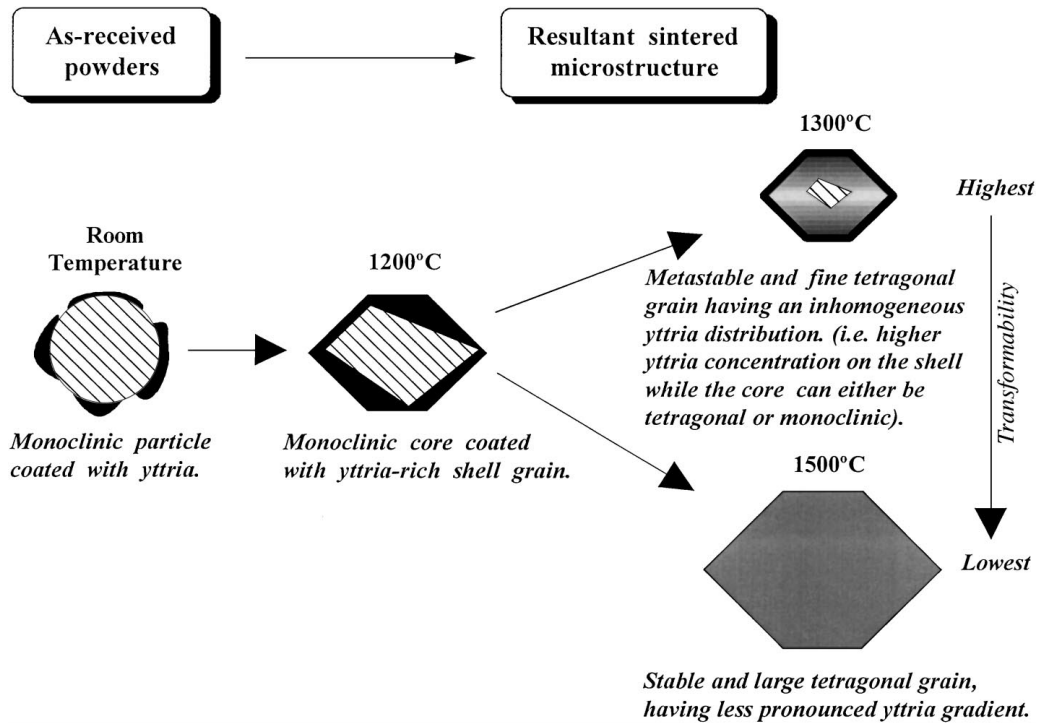


Figure 4 A schematic diagram depicting the behaviour of coated Y-TZP during sintering and the effect of sintering temperature on yttria distribution and transformability of the tetragonal grain.

The K_{Ic} values were observed to peak for a sintering temperature of 1300°C for the undoped and CuO-doped (up to 0.2 wt %) samples and at 1350°C for the 0.5 wt % CuO additions before decreasing with increasing sintering temperature. The reasons why values for 0.1 wt % CuO samples were lower than those for 0.05 and 0.2 wt % materials are not clear but may have been the result of variations between tough samples when small crack size differences produce noticeable changes in K_{Ic} values. The maximum measured K_{Ic} values at room temperature for each composition are shown in Table II.

The equation proposed by Niihara *et al.* [13] for Palmqvist crack systems has a limitation, i.e. the ratio of the crack length, ℓ , to half the indent diagonal, a , should be higher than 0.25 and not more than 2.5. In the present work because of the high toughnesses of the low addition CuO-doped samples, this ℓ/a ratio was not readily satisfied, (in many cases it was lower than 0.25). Therefore the K_{Ic} calculation was repeated for all samples using the relationships derived by Shetty *et al* [20] and shown in Table II:

$$K_{Ic} = 0.0937(H_v P/4\ell)^{1/2} \quad (3)$$

where the usual notations still apply as in Equation 1 and 2. Other toughness values in Table II were calculated using the equation of Antis *et al.* [21] which was recently modified by Kaliszewski *et al.* [22] to account for the effect of compressive stress due to the surrounding transformation zone:

$$K_{Ic} = 0.019P(E/H_v)^{1/2}/c^{3/2} \quad (4)$$

where c is the radial crack dimension measured from the centre of the indent impression (i.e. $c = a + \ell$) and all other notations remain unchanged as in Equation 1.

The results presented in Table II show considerable discrepancy among the three sets of results. For the first two methods i.e. Equation 1 and 3, the high fracture toughness values showed significant scattering. The relationship of Shetty gave K_{Ic} values higher than average, which were followed by those from using Niihara's equation whereas the Kaliszewski's equation gave a smaller scatter in the values. Nevertheless, it is apparent that in all cases the CuO-doped samples (up to 0.2 wt %) exhibited higher K_{Ic} values than the undoped material.

Optical microscopy observations of Vickers indentations in CuO-doped samples frequently revealed that

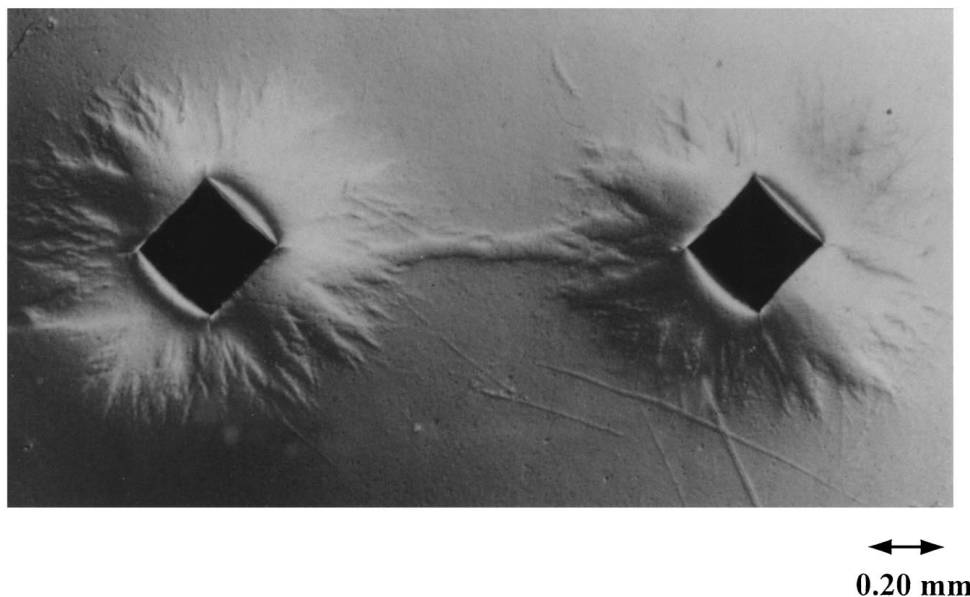


Figure 5 Normaski interference micrograph of typical Vicker's indents (load = 588 N) observed for 0.05 wt % CuO-doped Y-TZP, displaying significant transformation-induced surface uplift around indents at room temperature.

cracks, emanating from the indent corners, were very small and in extreme cases no cracks developed even at loads greater than 588 N. These effects were associated with surface uplift, due to the volume increase for the tetragonal-monoclinic phase transformation and consequently toughening, which occurred around the indents and which was revealed by Normaski lenses using polarised light as shown in Fig. 5. However an increase in the indentation load beyond 588 N, (in order to obtain an ℓ/a ratio valid for Niihara's equation), frequently resulted in surface spalling around the indent which made the determination of K_{Ic} impossible.

Vicker's hardness as a function of sintering temperature is shown in Fig. 6.

The additions of CuO up to 0.2 wt % exhibited higher hardness than the undoped ceramic throughout the sintering regime employed. Typical values measured for the CuO-doped samples varied from 10.5 to 12.8 GPa

and the measured hardnesses of all the samples revealed a similar trend, i.e. increasing with higher sintering temperatures. The hardness of the undoped Y-TZP ceramic was low when sintered at 1250 °C (9.13 GPa) but increased with sintering temperature to a maximum value of ~12.3 GPa for 1500 °C sintering. In general, the increase in hardness can be attributed to the increase in bulk density as shown in Fig. 2.

3.5. Microstructural evolution

Typical microstructures of the undoped and CuO-doped samples, sintered at 1300 and 1500 °C, shown in Fig. 7, exhibited equiaxed small tetragonal grains with small amounts of larger cubic grains, which were more noticeable for the higher sintering temperatures. One effect of CuO doping was to minimise the amount of cubic phase and reduce the average grain size of the sintered

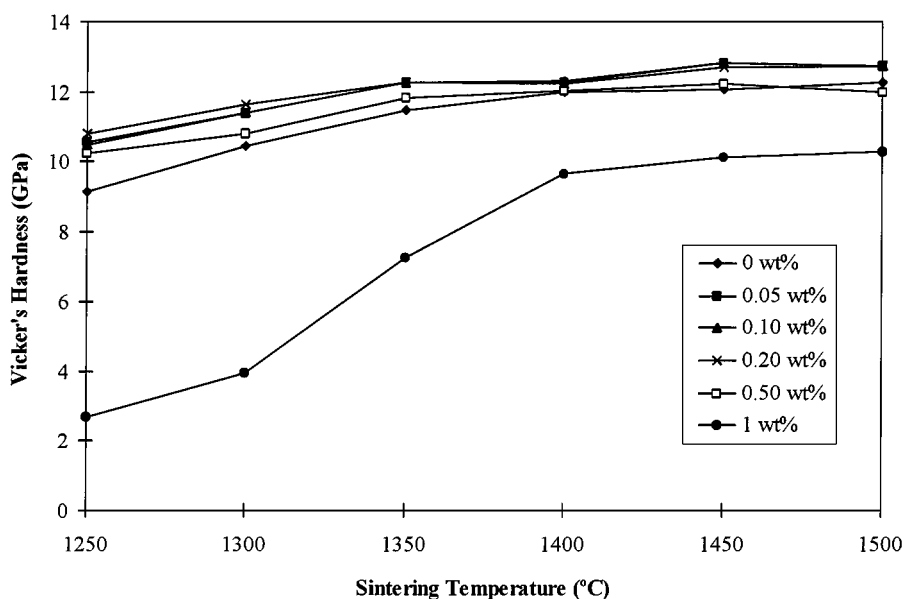


Figure 6 The effects of sintering temperature on the Vicker's hardness of undoped and CuO-doped Y-TZPs.

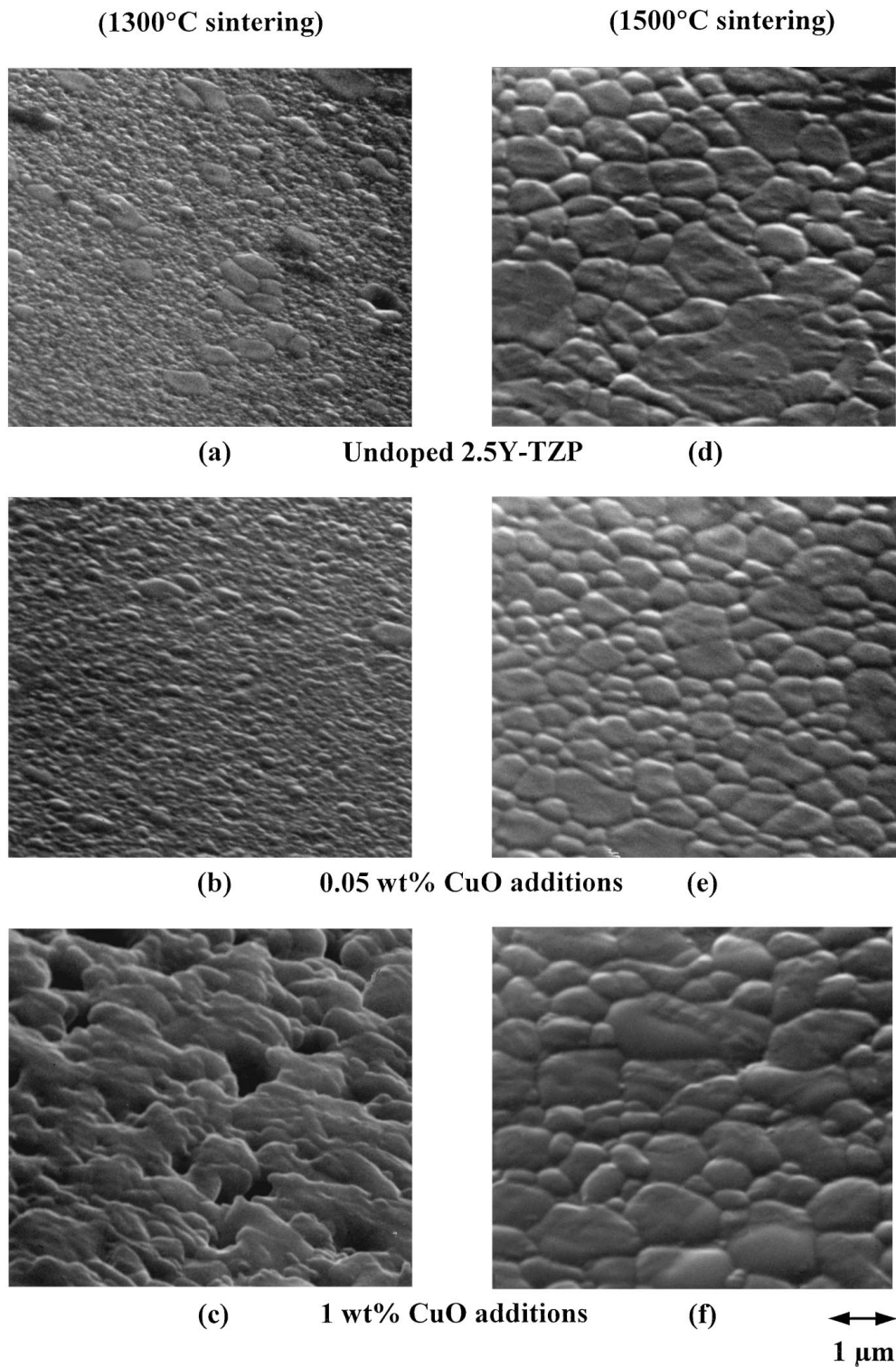


Figure 7 Microstructural evolution of undoped and CuO-doped 2.5Y-TZP ceramics sintered at 1300 °C and 1500 °C respectively.

body as compared to the undoped Y-TZP [5]. In general the average grain sizes for the doped material up to 0.5 wt % at a particular sintering temperature were similar and increases in size with sintering temperature were observed, Table III.

However, large amounts of CuO additions (1 wt %) especially at low sintering temperature (<1300 °C) resulted in the development of a porous structure which in part explains the low bulk density of this material, Fig 7c. In addition, occasionally rounded individual

TABLE III Comparison of the mean grain sizes (μm) of undoped and CuO-doped Y-TZPs

Sintering temperature (°C)	Undoped 2.5Y-TZP	0.05–0.5 wt % CuO additions	1 wt % CuO additions
1300	0.16	0.13–0.2	Porous structure
1350	0.24	0.16–0.25	Porous structure
1400	0.33	0.30–0.35	0.66
1450	0.51	0.40–0.45	0.72
1500	0.74	0.52–0.60	0.76

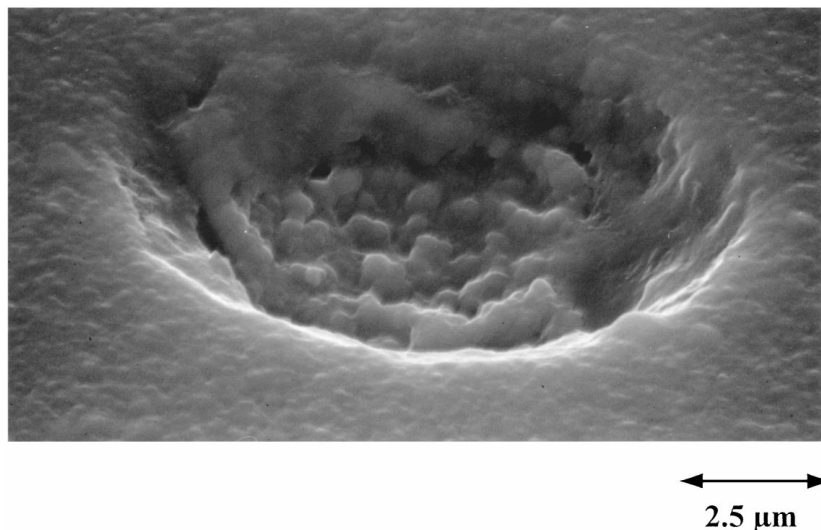


Figure 8 Typical pore morphology observed for CuO-doped Y-TZP. (In this case was 0.5 wt % CuO-doped sample sintered at 1350 °C).

large pores were noticed on the surfaces of CuO-doped samples (≤ 0.5 wt %) for sintering above 1300 °C (see Fig. 8) which indicates the presence of a liquid phase during sintering.

Seidensticker and Mayo [23] suggested that pressure build-up within closed pores would occur as a result of the decomposition of CuO to Cu₂O and oxygen, with the latter being evolved during sintering. These authors noticed that a sudden large weight loss took place at 1300 °C due to the evolution of half the oxygen from the decomposed CuO and the release of pressure build-up resulted in the formation of open pores. Zhang *et al.* [24] also noted that a weight loss caused by the reaction of CuO to Cu₂O increased with CuO content.

This development of spheroidal pores, Fig. 8, frequently observed for samples containing CuO additions and the porous structure, Fig. 7c, exhibited by the 1 wt % CuO addition Y-TZP at ≤ 1300 °C, support the observations of Seidensticker and Mayo about a liquid phase formation, the weight losses and gas evolution.

The porosity of the 1 wt % CuO doped samples, however, was noticed to diminish when the sintering temperature was increased above 1300 °C and a more dense structure formed as shown in Fig. 7c and f. Although some grain growth had occurred in the 1 wt % CuO-doped sample for the 1500 °C sintering, the average grain size of 0.76 μm was well below the critical grain size for high tetragonal phase retention for Y-TZP ceramics as shown in earlier research [5].

Therefore because of the large amount of monoclinic phase present in the structure accompanied by macro-cracking, it is postulated that the high concentration of CuO would have led to destabilisation of the tetragonal phase through a mechanism involving dissolution of yttria from the grains into a CuO-based grain boundary liquid.

It has been reported previously that CuO dissociates either at 1026 °C [24, 25] or 1031 °C [23] to form oxygen and Cu₂O which then melts at between 1134–1144 °C [26]. However, prior to the Cu₂O melting a eutectic occurs at 1130 °C [25] in the CuO-Cu₂O-ZrO₂ system and at 1110 °C [26] or 1120 °C [24] in the

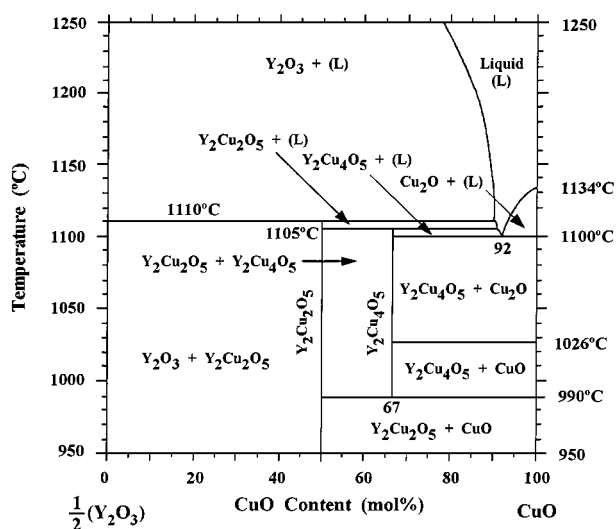


Figure 9 Pseudo-binary phase diagram of the Y₂O₃-CuO system in air. (After Gadalla and Kongkachuichay [26]).

Y₂O₃-CuO-Cu₂O system respectively. Zhang *et al.* [24] and Gadalla *et al.* [26] have reported the formation of Y₂Cu₂O₅ compound as a result of the reaction between Y₂O₃ and CuO but are in disagreement regarding the temperature at which this occurred. Nevertheless, both sets of authors agree that above the eutectic point, the Y₂Cu₂O₅ compound will melt to form Y₂O₃ and Cu-rich liquid. Besides the existence of Y₂Cu₂O₅ compound, Gadalla *et al.* found that an intermediate phase with the composition Y₂Cu₄O₅ coexists between 990–1105 °C and they constructed the pseudo-binary phase diagram of the Y₂O₃-CuO in air as shown in Fig. 9. This intermediate phase will also dissociate to form Y₂O₃ and liquid when heated above 1110 °C as shown schematically in Fig. 9.

Assuming in the present work that any one of these reactions occurred during the sintering of CuO-doped Y-TZP, then Fig. 9 indicates that as the sintering temperature increases there would have been more Y₂O₃ taken into solution by the Cu-rich liquid. For the lower CuO samples when the tetragonal phase was retained

to room temperature any removal of yttria into a grain boundary phase would act to enhance the transformation toughening and result in the very high K_{Ic} values observed in this work.

However, the role of this liquid phase is not unequivocally resolved as TEM examination [4, 8] of the CuO-doped samples has not revealed significant quantities remaining in grain boundary regions. The remnant Cu-rich liquid may have been too small to be detected or it may have had a solubility limit allowing diffusion into the zirconia grains. Hartmanova *et al.* [27] have proposed that CuO can dissolve in zirconia via substitutional doping due to the comparable ionic radius of both metal ions, i.e. $r_{Zr(IV)} = 0.084$ nm and $r_{Cu(II)} = 0.073$ nm respectively [28]. They also found that the grain size of the CuO-doped YSZ was larger than for the undoped ceramic. This solid solution behaviour may be more prevalent for the higher sintering temperatures. Further examination would be required to elucidate this phenomenon.

The additions of small amounts (0.3–1.0 mol %) of copper oxide to these ceramics were reported by some researchers to greatly enhance superplastic behaviour [9, 29, 30]. Hwang *et al.* [29] have shown clear evidence of the presence of a Cu-rich grain boundary layer (~ 1 – 2 nm thick) to which they attributed the improved superplastic deformation at temperatures < 1200 °C. This amorphous phase apparently melts at ~ 1130 °C which is in good agreement with temperatures found by other researchers [23].

Based on the present observations and evidence provided in the literature, it is proposed that a liquid phase is present during sintering of the CuO-doped Y-TZP ceramics. The following sintering model is tentatively proposed as one of mechanisms for the present CuO-doped coated 2.5Y-TZP powders: On heating to > 1100 °C, CuO will dissociate and form a molten cuprous oxide, Cu_2O based liquid phase at grain boundaries and the amount present is dependent on the CuO content in the powder. This Cu_2O liquid will dissolve Y_2O_3 to form either $Y_2Cu_2O_5$ or $Y_2Cu_4O_5$. For higher dopant levels, greater amounts of Cu_2O -rich liquid will be formed during sintering, resulting in more yttria being taken into solution. Therefore in the present work for the 1 wt % CuO additions, the amount of yttria remaining in the zirconia structure would have been reduced below the minimum limit for stabilisation to occur and on cooling after sintering, the tetragonal to monoclinic phase transformation would proceed.

Small amounts of CuO (i.e. below ~ 0.2 wt %) form a liquid phase which can act as a conduit allowing yttria re-distribution. Dissolution into the Cu-rich liquid will facilitate the re-distribution by diffusion of Y^{3+} into the zirconia grains resulting in the stabilisation of tetragonal phase in the ZrO_2 grains being achieved at low sintering temperatures, (≤ 1300 °C). In this way an yttria gradient across grains is established giving easy stress-induced phase transformation, hence accounting for the high toughness of this material.

3.6. Hydrothermal ageing

The phase stabilities of the undoped coated 2.5Y-TZP (0 wt %) and CuO-doped (up to 0.2 wt %) coated 2.5Y-

TZP materials, all sintered at 1300 °C, were studied by exposure in superheated steam at 180 °C in an autoclave operating at 1 MPa for up to 200 h.

A comparison was also made with undoped co-precipitated 3 mol % Y-TZP material (TZ-3Y) manufactured by the Tosoh Corporation of Japan which was sintered at 1400 °C. The co-precipitated 3Y-TZP was chosen for this work instead of 2.5Y-TZP since it has been found in the past that the latter ceramic was more susceptible to hydrothermal ageing and failed catastrophically in the early stages of exposure [31].

The measured room temperature properties of the sintered TZ-3Y samples at the start of this work were as follows: 100% tetragonal phase content, bulk density of 6.07 Mgm^{-3} , average grain size of 0.33 μm , K_{Ic} of 5.1 $MPam^{1/2}$ and H_v of 13.9 GPa respectively. The coated and doped 2.5Y-TZP materials were of similar density to the Tosoh specimens but had lower grain sizes, 0.16 – 0.20 μm .

The development of monoclinic phase with time in these zirconias when exposed to high pressure steam at 180 °C is shown in Fig. 10. Both of the undoped samples (coated 2.5Y-TZP and TZ-3Y) exhibited inferior resistance to ageing when compared to the lower CuO-doped materials and the ageing-induced tetragonal to monoclinic phase transformation proceeded at different rates. TZ-3Y ceramics degraded almost immediately when exposed to water and attained a monoclinic saturation level of $\sim 89\%$ within 9 h before breaking into pieces after ageing for 24 h. In contrast, the undoped coated 2.5Y-TZP ceramic was more resistant to degradation than the TZ-3Y and exhibited slower ageing kinetics, acquiring a monoclinic saturation level of $\sim 80\%$ after 100 h of exposure and surviving throughout the test.

The better ageing resistance of coated Y-TZP is attributed to the inhomogeneous yttria distribution in the ZrO_2 grains. The enrichment of stabiliser at the rim of the grain would have over stabilised these regions creating stable tetragonal (or cubic) shells surrounding metastable grain cores. During ageing monoclinic nucleation would have initiated in the central regions of surface grains due to their low yttria content. Once initiated, further ageing would allow the growth of these monoclinic nuclei until the core regions were almost completely transformed. The shell of a grain being more stable (with a higher yttria content) would have required longer exposure times to water attack before it started to transform. The fact that the coated Y-TZP ceramics still remained intact even after autoclaving for up to 200 h while TZ-3Y degraded quickly, supports this view. It should be noted that although coated Y-TZP powder possessed better ageing resistance than co-precipitated powders, the initiation of monoclinic nuclei resulting from hydroxyl attack was not totally prevented.

For the CuO doped materials, the best ageing resistance was exhibited by the 0.05 wt % addition samples (exhibiting $< 40\%$ monoclinic content after 200 h). The 0.1 wt % CuO dopant sample exhibited reasonably good resistance in the early stages of exposure (< 50 h) if compared to the undoped Y-TZPs (see Fig. 10). Although the 0.2 wt % CuO addition sample exhibited lower initial ageing kinetics than the undoped coated

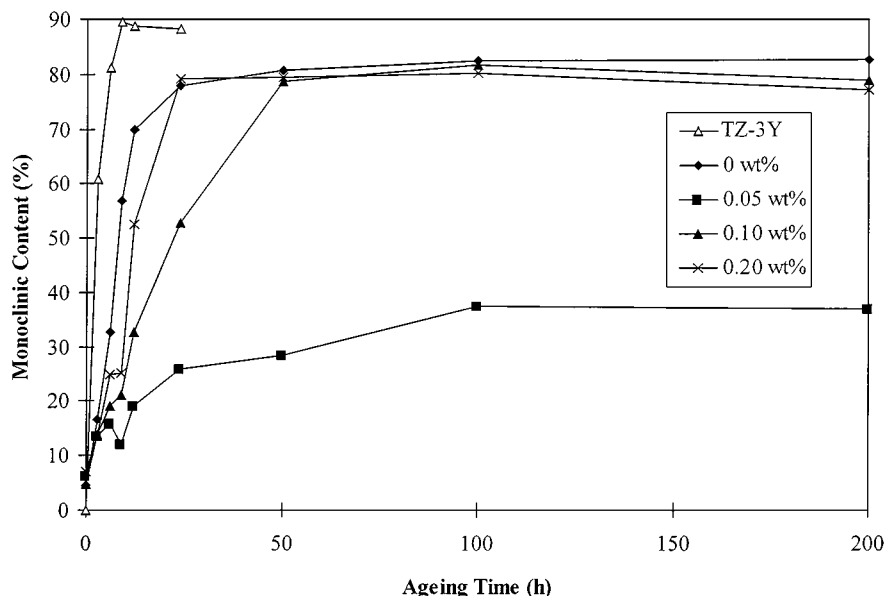


Figure 10 The surface monoclinic content development with ageing time for undoped and CuO-doped Y-TZP ceramics when exposed in superheated steam at 180 °C and 1 MPa pressure.

Y-TZP ceramic during the first 24 h of exposure, both the samples attained monoclinic saturation levels at about the same time, i.e. after 50 h. The final monoclinic contents attained in the undoped, 0.1 and 0.2 wt % CuO-doped samples after 200 h of exposure were almost the same, i.e. ~80–82%.

The benefits of CuO dopants in suppressing the ageing-induced phase transformation in other environments have been revealed and these results are presented elsewhere [8, 32, 33].

The role of the CuO dopant in retarding the ageing kinetics of Y-TZP ceramics is still debatable but is in part attributed to the small grain size of the sintered material resulting from low temperature sintering and grain boundary modification. The presence of CuO at grain boundaries has been found to be beneficial in retarding the propagation of monoclinic nuclei [8] and this will be reported in a subsequent paper.

Although a considerable effort has been directed towards resolving the ageing phenomenon of Y-TZP ceramics, no consensus has been reached regarding the ageing mechanism which is still the subject of debate.

4. Conclusions

(1) The incorporation of copper oxide can either be beneficial or detrimental to the sintering of coated 2.5 mol % Y-TZP depending on the dopant level.

(2) Additions of up to 0.2 wt % CuO are beneficial in achieving high levels of densification ($>6 \text{ Mgm}^{-3}$), high tetragonal phase retention ($>95\%$) and small grain sizes ($<0.25 \mu\text{m}$) at sintering temperatures lower than those required for the undoped Y-TZP.

(3) An optimum CuO dopant addition of $<0.5 \text{ wt } \%$ exists above which there can be detrimental effects for Y-TZP ceramics, with low bulk densities and high monoclinic phase content.

(4) The measured K_{Ic} for the CuO-doped samples containing less than 0.2 wt % using a conventional indentation method and calculated using three different equations gave very high average values ranging from

17 to 29 $\text{MPam}^{1/2}$. The enhanced transformability of the tetragonal grains as a result of small amounts of yttria dissolution into the Cu-rich liquid during sintering is in part responsible for the high fracture toughness of this material. Although no other methods were used to confirm the fracture toughness of the lower CuO-doped samples, the results reported in this work provide a good indication of one of the beneficial effects of CuO additions to coated 2.5 mol % Y-TZP powders.

(5) The hardnesses of the CuO-doped samples containing $<0.5 \text{ wt } \%$ are generally higher than for the undoped ceramics for all sintering temperatures. In general, the increase in hardness can be attributed to the increase in bulk density of the sintered body.

(6) A sintering mechanism involving a liquid phase resulting from the reaction between CuO and Y_2O_3 forming a liquid at the sintering temperature has been proposed for the CuO-doped coated Y-TZP system. This model is consistent with the phenomenological observations of sintering behaviour in terms of densification, mechanical properties and microstructural evolution.

(7) The addition of CuO as dopant in coated Y-TZP ceramics can have two extremes: Low additions of CuO are beneficial in aiding densification for low temperature sintering and to develop a tough material. High additions of CuO are detrimental to the sintered properties mainly due to greater amounts of yttria dissolution resulting in destabilisation of the tetragonal phase.

(8) Low temperature degradation associated with ageing-induced tetragonal-monoclinic phase transformation of Y-TZP ceramics can be suppressed with low additions of CuO attributable in part to the small grain size developed in the sintered body resulting from low temperature sintering and grain boundary modification via the presence of CuO dopant.

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References

1. I. MASAKI and K. KOBAYASHI, in "Advanced Ceramics," edited by S. Saito (Oxford Uni. Press, UK, 1988) pp. 210–226.
2. S. LAWSON, C. GILL and G. P. DRANSFIELD, *J. Mater. Sci.* **30** (1995) 3057–3060.
3. P. KOUNTOUROS and G. PETZOW, in "Science and Technology of Zirconia V," edited by S. P. S. Badwal, M. J. Bannister and R. H. J. Hannink (Technomic, Pub. Co. Inc., 1993) pp. 30–48.
4. S. LAWSON, PhD thesis, University of Sunderland, UK, 1993.
5. S. RAMESH, C. GILL, S. LAWSON and G. P. DRANSFIELD, *J. Mater. Sci.* **31** (1996) 6055–6062.
6. S. LAWSON, *J. Eur. Ceram. Soc.* **15** (1995) 485–502.
7. N. KIMURA, S. ABE, Y. HAYASHI, J. MORISHITA and H. OKAMURA, *Sprechsaaal* **122** (1989) 341–343.
8. S. RAMESH, PhD thesis, University of Sunderland, England, UK, 1997.
9. J. R. SEIDENSTICKER and M. J. MAYO, *Mater. Sci. Forum.* **170–172** (1994) 415–420.
10. L. A. XUE, *J. Mater. Sci. Letts.* **11** (1992) 1395–1397.
11. G. P. DRANSFIELD, in "Engineering Ceramics: Fabrication Science and Technology," Br. Ceram. Proc., Vol. 50, edited by D. P. Thompson (The Institute of Materials, London, 1993) pp. 1–8.
12. H. TORAYA, M. YOSHIMURA and S. SOMIYA, *J. Amer. Ceram. Soc.* **67** (1984) C-183–C-184.
13. K. NIIHARA, R. MORENA and D. P. H. HASSELMAN, *J. Mater. Sci. Letts.* **1** (1982) 13–16.
14. A. G. EVANS and E. A. CHARLES, *J. Amer. Ceram. Soc.* **59** (1976) 371–372.
15. M. I. MENDELSON, *ibid.* **52** (1969) 443–446.
16. S. LAWSON, G. P. DRANSFIELD, A. G. JONES, P. MCCOLGAN and W. M. RAINFORTH, in the 8th CIMTEC World Ceramics Congress, Florence, Italy, 1994.
17. W. E. LEE and W. M. RAINFORTH, "Ceramic Microstructures: Property Control by Processing" (Chapman and Hall, London, 1994) pp. 317.
18. M. L. MECARTNEY, *J. Amer. Ceram. Soc.* **70** (1987) 54–58.
19. M. GUST, G. GAO, J. WOLFENSTINE and M. L. MECARTNEY, *ibid.* **76** (1993) 1681–1690.
20. D. K. SHETTY, I. G. WRIGHT, P. N. MINCER and A. H. CLAUER, *J. Mater. Sci.* **20** (1985) 1873–1882.
21. G. R. ANTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64** (1981) 533–538.
22. M. S. KALISZEWSKI, G. BEHRENS, A. H. HEUER, M. C. SHAW, D. B. MARSHALL, G. W. DRANSMANN, R. W. STEINBRECH, A. PAJARES, F. GUIBERTEAU, F. L. CUMBRERA and A. DOMINGUES-RODRIGUEZ, *ibid.* **77** (1994) 1185–1193.
23. J. R. SEIDENSTICKER and M. J. MAYO, *ibid.* **79** (1996) 401–406.
24. W. ZHANG and K. OSAMURA, *Metall. Trans.* **21A** (1990) 2243–2248.
25. A. M. GADALLA and J. WHITE, *Trans. Brit. Ceram. Soc.* **65** (1966) 383–390.
26. A. M. GADALLA and P. KONGKACHUICHAY, *J. Mater. Res.* **6** (1991) 450–454.
27. M. HARTMANOVA, F. W. POULSEN, F. HANIC, K. PUTYERA, D. TUNEGA, A. A. URUSOVSKAYA and T. V. ORESHNIKOVA, *J. Mater. Sci.* **29** (1994) 2152–2158.
28. R. D. SHANNON, *Acta Cryst.* **32A** (1976) 751–767.
29. C.-M. J. HWANG and I-W. CHEN, *J. Amer. Ceram. Soc.* **73** (1990) 1626–1632.
30. J. R. SEIDENSTICKER and M. J. MAYO, *Scripta Metallurgica et Materialia* **31** (1994) 1749–1754.
31. S. RAMESH, Unpublished research, University of Sunderland, UK, 1995.
32. S. RAMESH, C. GILL, S. LAWSON and G. P. DRANSFIELD, in the Pacific Rim 2, International Ceramic Conference, Cairns, Australia, 1996, Paper no. 555.
33. C. GILL, S. RAMESH, C. Y. TAN, S. LAWSON and G. P. DRANSFIELD, in the Pacific Rim 2, International Ceramic Conference, Cairns, Australia, 1996, Paper no. 204.

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