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Environmental degradation of CuO-doped Y-TZP ceramics

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Abstract

The phase stabilities of plain and CuO-doped (up to 0.2 wt.%) coated 2.5 mol% Y-TZP ceramics, sintered at 1300°C, were investigated by exposure in hostile environments for periods of up to 2000 h. CuO additions significantly reduced the rate of tetragonal to monoclinic phase transformation compared with that for undoped samples. In addition the mechanical properties of the doped materials were better in all cases. Specimen sectioning, however, revealed that after 200 h even the samples with CuO had developed thin, measurable monoclinic layers. Doping of Y-TZP ceramics with small amounts of CuO is one method of reducing ageing degradation without sacrificing other properties. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Environmental degradation; CuO-doped; Y-TZP ceramics

1. Introduction

Zirconia-based materials are increasingly being considered in engineering applications as alternatives to other ceramic materials due to their relatively high fracture toughnesses and bending strengths. Values of fracture toughness of greater than 12 MPa $m^{1/2}$ and tensile strengths of 1000–1500 MPa have been observed for 2.5 mol% yttria-stabilised zirconia [1,2] as compared with alumina [3] which exhibited a low fracture toughness (<5 MPa $m^{1/2}$) and a low bending strength (<600 MPa). In addition the atomic defects (i.e. oxygen vacancies) created in zirconia due to doping with lower-valent cations such as yttrium in order to stabilise the high temperature polymorphs allow the migration of oxygen ions [4]. Hence zirconia-based ceramics possess excellent ionic conductivity. 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 and cutting tools [5–9].

Yttria-tetragonal zirconia polycrystals ceramics (Y-TZP) possess excellent strength and high fracture toughness 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. The effectiveness of this mechanism is dependent on the processing history of the powders which has a significant influence on the sintered microstructure and mechanical properties of the resulting body. It was shown in previous work [10,11] that 2.5 mol% Y-TZP materials consisting of small (t) 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 (t) 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 MPa $m^{1/2}$, respectively). On the other hand the fracture toughness of the equivalent co-precipitated Y-TZP ceramics increased with increasing grain size (e.g. for grains of 0.38 and 0.98 μm fracture toughnesses of 5 and 10.2 MPa $m^{1/2}$, respectively were measured).

One of the major limitations of Y-TZP ceramics as engineering materials is the undesirable surface-initiated phase transformation from the (t) to (m) symmetry accompanied by property degradation during exposure to low temperature water or aqueous solutions [12]. The underlying mechanism is still under debate but it is understood to be associated with hydroxyl ion incorporation in the zirconia lattice, which subsequently destabilises the tetragonal phase.

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The inclusion of liquid forming additives in Y-TZP powders, in particular of transition metal oxides [2,13,14], is likely to affect hydrothermal ageing resistance if they aid sintering at relatively low temperatures (i.e. $\leqslant 1300°C$) and result in densification without grain growth.

The aims of the present work were to study the effects of doping coated 2.5 mol% Y-TZP ceramics with small amounts of copper oxide on the room temperature mechanical properties and phase stability during exposure in hostile environments.

2. Materials and methods

2.1. Sample preparation

The 2.5 mol% yttria-coated zirconia powder supplied by Tioxide Specialties Ltd, UK, were prepared by synthesis of ZrO_2 in a plasma reactor, rapid cooling and coating with yttria in a process described elsewhere [15]. 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 and 0.2 wt.%) were mixed in an attritor-mill containing the undoped Y-TZP powder, distilled water and 1 mm diameter Y-TZP milling balls. The speed of the rotation was kept constant at $\sim$1960 rpm and each milling was carried out for half an hour prior to filtration.

After the mixing process, the slurries were separated from the milling media by filtration using a standard 150 μm mesh sieve and washed with distilled water. The slurries were then deflocculated with 35 wt.% ammonia solutions until a pH of >10 was obtained prior to the drying process which was carried out overnight in an oven at 110°C.

Finally, dried powders were obtained by sieving using a 125 μm mesh sieve. Disc samples (19 mm diameter and weighing $\sim$3 g) were made by uniaxial pressing at 35 MPa followed by cold isostatic pressing at 200 MPa. All the samples were sintered for 2 h at 1300°C at a ramp rate of 10°C/min. The sintered samples were polished on one face to a 1 μm surface finish prior to testing.

2.2. Characterization

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 using Cu-K_α as the radiation source. The fraction of surface monoclinic content was evaluated using the method of Toraya et al. [16]. Fracture toughness (K_{IC}) and microhardness (H) were measured on polished samples using the Vicker's indentation method at a constant load of 490 N. It should be emphasised here that the indentation test employed to determine the K_{IC} was used solely for comparative purposes as a tool to evaluate the effects of variations in processing parameters and CuO additions. The K_{IC} was computed according to the equation derived by Antis et al. [17] which was recently modified by Kaliszewski et al. [18] to account for the effect of compressive stress due to the surrounding transformation zone:

$$K_{IC} = 0.019P(E/H)^{1/2}/c^{3/2} \tag{1}$$

$$H = \frac{1.854P}{(2a)^2} \tag{2}$$

where P is the indentation load, E the Young's modulus, H is the Vicker's hardness, a the indent half diagonal, c the radial crack dimension measured from the centre of the indent impression (i.e. $c = a + \ell$) and ℓ is the average crack length. Six measurements were made for each sample and average values were obtained.

The grain size was determined on thermally etched specimens from scanning electron micrographs using the line intercept analysis of Mendelson [19]. The hydrothermal ageing was performed in an autoclave containing superheated water at 180°C (1 MPa) for up to 200 h. The acidic corrosion was under refluxing conditions in 20% hydrochloric acid at 110°C and comparisons were made with the behaviour when the acid was replaced by distilled water. Samples were also exposed in hot air at 180°C for periods ranging up to 2000 h. The degradation was assessed by monitoring changes in surface monoclinic content, weight and density. In addition, all the hydrothermally aged samples were sectioned to measure the transformed monoclinic layer depth.

3. Results and discussion

3.1. Properties of as-sintered samples

The results in Table 1 clearly show the beneficial effects of incorporating small amounts of CuO in 2.5Y-TZP ceramics. In general, all of the doped samples exhibited higher bulk densities (>6 Mg m^{-3}) and high fracture toughnesses (>17 MPa m$^{1/2}$) if compared to the undoped ceramics.

The unique combination of high toughness and small grain size exhibited by the undoped and CuO-doped ceramics can be attributed to:

1. the stabiliser distribution within the powder resulting in yttria enrichment at the outer grain regions of the sintered body [10,11];
2. the additions of CuO enhance this phenomenon by forming Y/CuO at the grain boundaries thus effectively leading to high toughness ceramics [11].

Table 1
Properties of sintered (1300°C) Y-TZPs

CuO content	Tetragonal content (%)	Bulk density (Mg m^{-3})	K_{IC} (MPa $m^{1/2}$)	H (GPa)	Average grain size (μm)
Undoped	97	5.91	15.46 ± 0.37	10	0.16
0.05 wt.%	98	6.03	19.20 ± 0.99	11	0.13
0.10 wt.%	98	6.03	17.21 ± 0.56	11	0.14
0.20 wt.%	98	6.03	18.76 ± 1.38	11	0.15

A schematic diagram showing the effect of powder processing route and sintering temperatures on the microstructure and transformability of the (t) grains in coated Y-TZP ceramics is presented in Fig. 1.

As for the doped system, small amounts of CuO (up to 0.2 wt.%) could have caused some redistribution of yttria to occur, thereby reducing the concentration of the stabiliser in the shell of the ZrO_2 grains relative to that in the undoped material. As a result, the overall yttria content in the grains would have decreased as some yttria would have been taken into solution with the CuO-rich liquid, the amount of which is not below some critical level required for stabilisation to occur. Therefore, this small overall reduction in stabiliser contents in the CuO-doped ceramics would have enhanced the transformability of the grains at lower temperatures. This in turn would have caused the stress field of a propagating crack to be more readily accommodated in the tetragonal grains of the doped samples than in the undoped ceramics i.e. enhanced the transformation toughening effect.

3.2. Effects of hostile environments on tetragonal phase stability

3.2.1. Hydrothermal degradation

The development of the monoclinic phase with time when exposed to high pressure steam at 180°C is shown in Fig. 2. The undoped Y-TZP exhibited inferior resistance to ageing when compared to the 0.05 wt.% CuO-doped sample and the ageing-induced (t) to (m) phase transformation proceeded at different rates.

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 ageing resistance in the early stages of exposure (< 50 h) compared to the undoped Y-TZP (see Fig. 2). Although the 0.2 wt.% CuO addition sample exhibited lower initial ageing kinetics than the undoped coated Y-TZP ceramic during the first 24 h of exposure, both the samples attained monoclinic saturation levels at about the same time. The saturation monoclinic contents attained in the

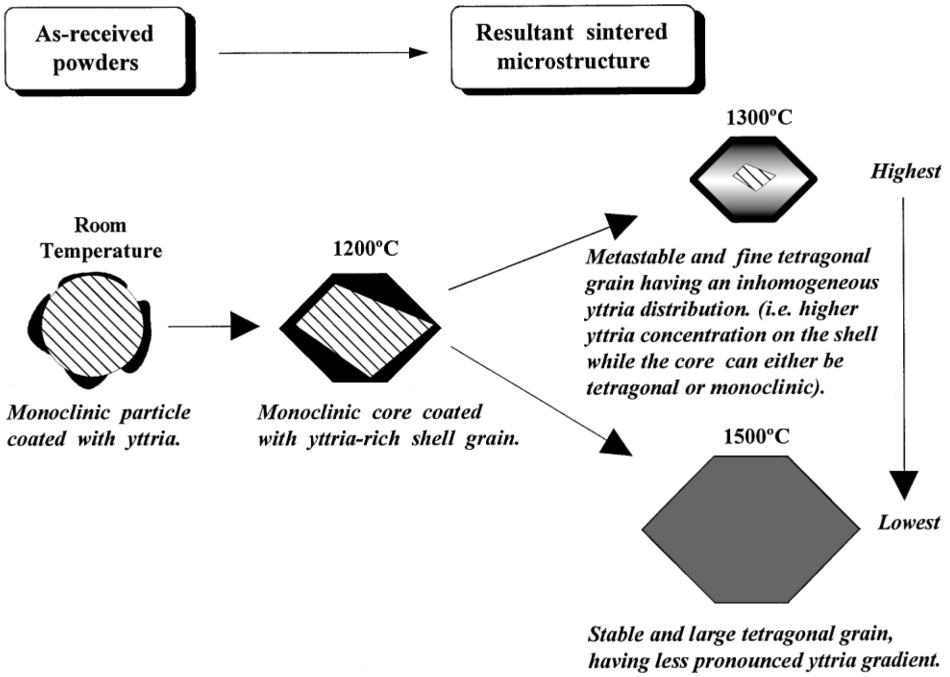

Fig. 1. A schematic diagram depicting the behaviour of coated Y-TZP during sintering and the effect of sintering temperature on yttria distribution and transformability of the tetragonal grain.

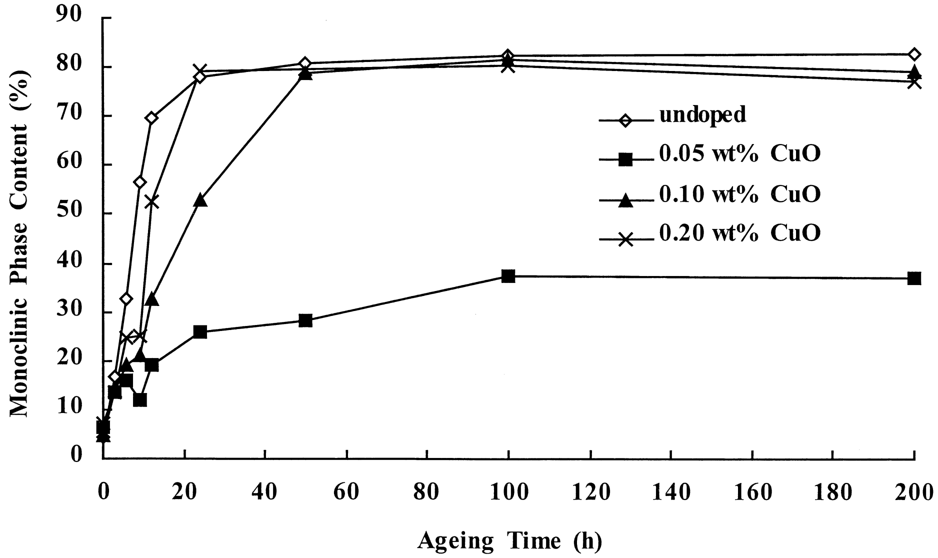

Fig. 2. The effects of CuO additions on the hydrothermal ageing behaviour (180°C and 1 MPa) in coated Y-TZPs. All samples were sintered at 1300°C.

undoped, 0.1 and 0.2 wt.% CuO-doped samples after 200 h of exposure were similar, i.e. about 80–82%.

The increase in monoclinic phase content with increasing CuO content was expected. It has been postulated previously [14] that the reduction in yttria enrichment at grain boundary regions as a result of increasing yttria dissolution into the CuO-rich phase due to increasing CuO contents would have lowered grain boundary resistance to water attack. However, small amounts of yttria dissolution as in the case of 0.05 wt.% CuO additions were beneficial in terms of transformation toughening and also for grain boundary modification. The contribution of grain size is another factor. Small differences in size i.e. 0.13 μm for 0.05 wt.% CuO-doped material compared with 0.15 μm for 0.2 wt.% CuO-doped samples showed a significant effect on the hydrothermal ageing behaviour. However, it is believed that the grain size was not the salient factor controlling the ageing behaviour of the CuO-doped Y-TZPs.

3.2.2. Refluxing conditions in 20% HCl solutions and boiling distilled water

The effects of refluxing in 20% hydrochloric acid at 110°C and boiling distilled water at 100°C on the monoclinic phase development with time are shown in Figs. 3 and 4 respectively.

In general, both graphs show that the CuO additives were beneficial in retarding the (t) to (m) phase

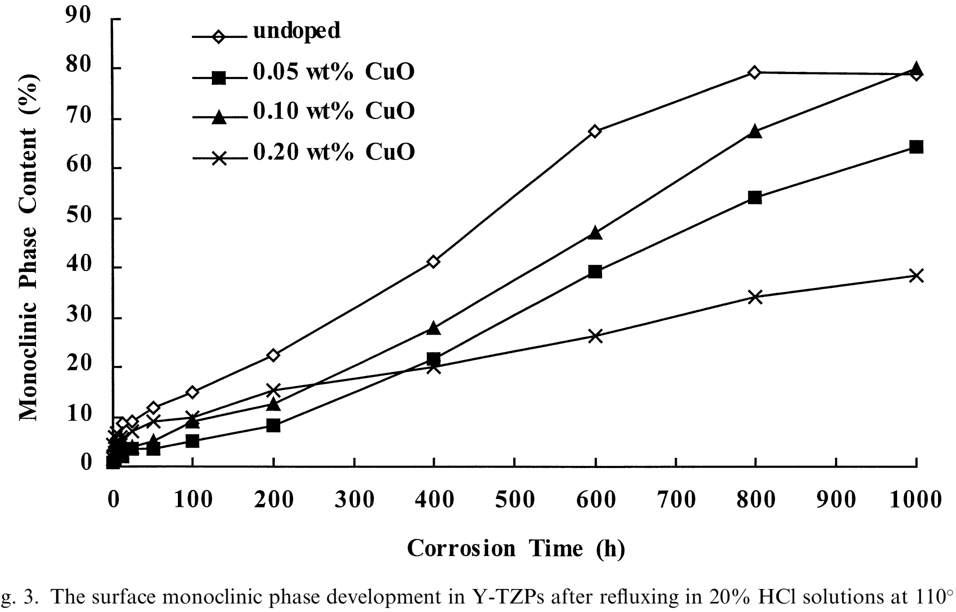

Fig. 3. The surface monoclinic phase development in Y-TZPs after refluxing in 20% HCl solutions at 110°C.

transformation when compared to the undoped material. It is interesting to note that the after 400 h of exposure, the higher CuO-doped Y-TZP (i.e. 0.2 wt.%) exhibited better resistance to acid corrosion than when exposed in boiling water or superheated steam. As for the 0.05 and 0.1 wt.% CuO-doped samples, the monoclinic phase development with time seemed to proceed at similar rates with the former being less vulnerable to ageing-induced (t) to (m) phase transformation (see Figs. 3 and 4).

The poor corrosion resistance of Y-TZP was mainly due to attack near grain boundary regions resulting in destabilisation of the (t) phase thereby inducing the phase transformation to (m) structure [10,14,20,21].

Since it is postulated that the yttria enrichment factor near grain boundaries would be reduced with increasing CuO-content and the corrosion results revealed that such samples (i.e. 0.2 wt.% CuO-doped) had better corrosion resistance, it is suggested that a mechanism involving reaction with yttria at or near grain boundaries is responsible for the degradation process. The fact that the undoped sample (which had a higher intragranular Y_2O_3 gradient) exhibited the poorest corrosion resistant supports this view. The possibility has not been ruled out that during ageing or corrosion, the hydroxyls from the medium could react with Y_2O_3 along grain boundary regions to form Y-OH bonds. Thus, the

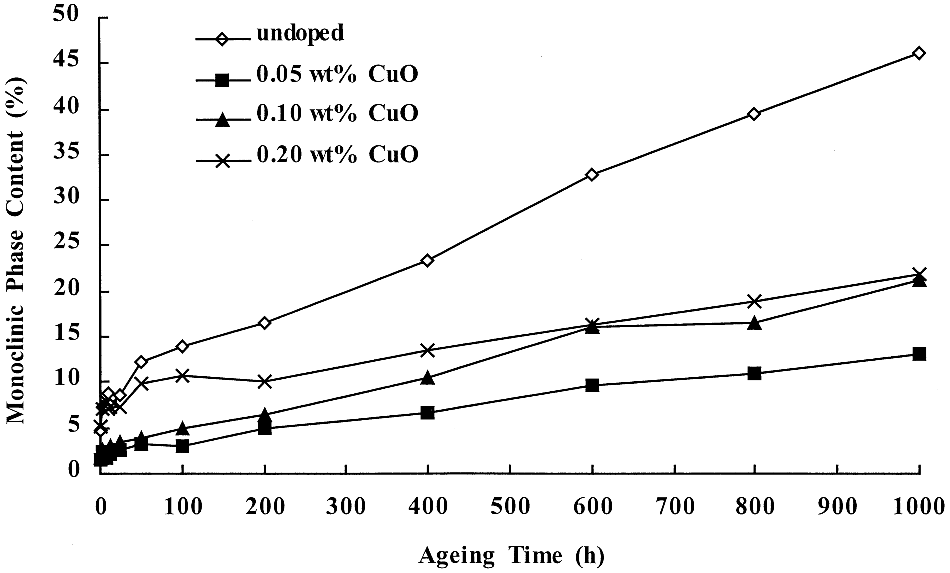

Fig. 4. The effects of refluxing Y-TZPs in boiling distilled water at 100°C on the monoclinic phase development.

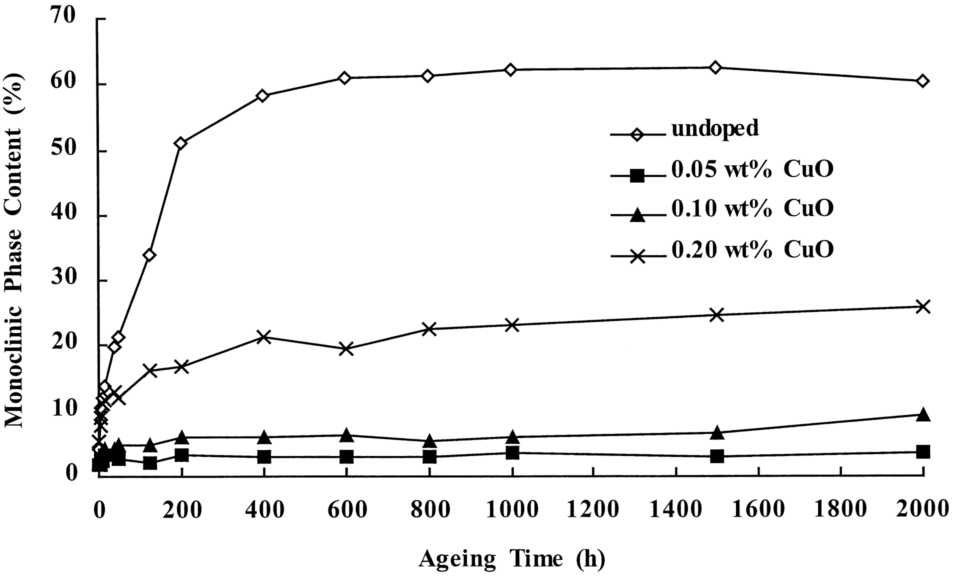

Fig. 5. The effects of ageing in hot air at 180°C on the monoclinic phase development in Y-TZPs.

presence of a CuO–Y_20_3 phase at grain boundary regions would prevent the OH reaction with Y, therefore, enhancing corrosion resistance.

3.2.3. Ageing in hot air at 180°C

The effects of ageing in hot air at 180°C on the tetragonal phase stability in Y-TZPs are shown in Fig. 5.

Transformation from tetragonal to monoclinic phase has been attributed at least in part to the action of moisture but these present results show that in undoped Y-TZP which had the highest yttria concentration near grain boundary regions developed a high monoclinic content. In contrast, the copper oxide doped ceramics exhibited better resistance to phase transformation even after 2000 h of exposure. In particular, samples containing 0.05 wt.% CuO exhibited the least phase transformation i.e. developing less than 4% monoclinic phase after 2000 h. Similar observations were also noted for the 0.1 wt.% CuO-doped samples which had developed $<10\%$ (m) content. The rate of surface monoclinic phase development in the 0.2 wt.% CuO-doped samples was observed to increase with time during the early hours of exposure before remaining constant after 800 h, developing ~26% monoclinic content.

These observations clearly suggest that a reaction involving yttria near grain boundary regions was responsible for the degradation. It is hypothesised that there exist a certain critical amount of yttria concentration (Y_{cr}) near grain boundary regions which controls the monoclinic nucleation and subsequently the rate of degradation in the zirconia. For instance, in the undoped ceramics, the Y concentration near grain boundary regions was expected to be greater than Y_{cr} but the ageing resistance of the ceramics was not improved when samples were exposed in hostile environments. On the other hand, in the case of the 0.2 wt.% CuO-doped ceramics, the Y concentration near grain boundary regions would be expected to be lower than in the 0.05 wt.% CuO-doped materials and Y_{cr} as a result of more yttria being taken into solution with the Cu-rich liquid during sintering. This in turn would lower the tetragonal grain resistance to water and the barrier for phase transformation to proceed would be lowered thus permitting monoclinic nucleation.

In contrast, the yttria concentration near grain boundary regions in the 0.05 wt.% CuO-doped materials would be expected to be lower than that in the undoped ceramics but higher than in the 0.2 wt.% CuO-doped samples. Since the 0.05 wt.% CuO-doped Y-TZP showed the overall best anti-degradation property, it is suggested that some minimum amount of yttria concentration near grain boundary regions was beneficial in retarding the phase transformation. However, more work is in progress to elucidate the actual mechanism. The exact role of CuO–Y_2O_3 grain boundary phase during ageing is still to be resolved but it is believed that the formation of compounds could have prevented further hydroxyl reaction with Y near grain boundary regions.

3.2.4. Monoclinic layer thickness

Further evidence of the efficacy of CuO dopants in retarding the (t) to (m) phase transformation in Y-TZPs was obtained by sectioning the hydrothermally aged samples at each exposure time interval and the (m) layer being measured. The monoclinic layer thickness measurements revealed that all the CuO-doped samples had

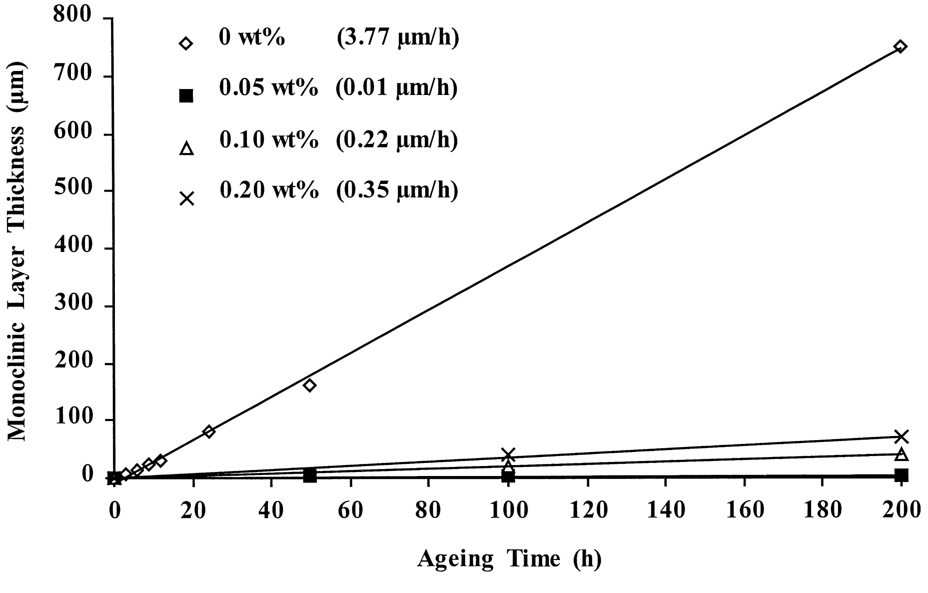

Fig. 6. The effects of CuO additions on the (m) layer thickness with respect to time for samples aged in superheated steam at 180°C and 1 MPa. The (m) layer propogation rate is given in parentheses.

very thin monoclinic layers which developed even after 200 h of ageing, see Fig. 6. The addition of 0.05 wt.% CuO was very effective in retarding the (m) layer propagation rate by a factor of more than 300 as indicated in parentheses in Fig. 6.

4. Conclusions

1. The additions of small amounts of CuO (up to 0.2 wt.%) to coated 2.5 mol% Y-TZP were found to be beneficial as a sintering aid. The bulk densities of all the doped samples were higher (>6 Mg m^{-3}) than for the undoped ceramics when sintered at 1300°C.
2. The fracture toughnesses of the CuO-doped Y-TZPs were also generally higher than the undoped material and was in-part attributed to the inhomogeneous distribution of yttria in the structure.
3. The environmental degradation phenomenon of Y-TZP ceramics as a result of (t) to (m) phase transformation was suppressed via the additions of CuO dopant.
4. Y-TZPs doped with 0.05 wt.% CuO had more effective resistance to the ageing-induced (t) to (m) phase transformation in environments containing 100% water and in hot air. In contrast samples containing 0.2 wt.% CuO were more resistant to degradation in corrosive environment such as in 20% HC1 solutions.
5. Dissolution of yttria near grain boundary regions as a result of water reaction was responsible for triggering the monoclinic nucleation.

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