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Hydrothermal ageing of yttria-stabilised zirconia, sintered at 1300°C–1325°C: the effects of copper oxide doping and sintering time variations

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Co-precipitated yttria-stabilised zirconia powders were doped with 0.05% wt of copper oxide (CuO). Samples were sintered at 1300°C–1325°C with holding times varying from 12 mins up to 4 hrs. The material was stable when exposed to hydrothermal ageing at 180°C, with only minimal signs of degradation in many cases for in excess of 3000 hrs. Excellent ageing resistance was observed for samples doped with 0.05 wt% of CuO, sintered at 1315°C for 12 mins which developed less than 1% monoclinic phase content, after 5000 hrs. Samples doped with 0.05 wt% of CuO, sintered at 1325°C for 12 mins, developed more than 50% of surface monoclinic phase content after 800 hrs of ageing, maintaining the same amount of monoclinic phase content for in excess of 3000 hrs. Plain samples sintered at 1325°C for 2 hrs developed more than 30% monoclinic phase content after 750 hrs. Doping with CuO improved the ageing resistance of the samples sintered at 1300°C–1315°C for 2 hrs and 12 mins holding times respectively.

1. Introduction

Zirconia ceramics have been used for many years in various demanding applications including cutting tools, grinding media, knives, scissors, crucibles, thermal barrier coatings, heating elements, coatings, fuel cells, insulators, roller guides, extrusion dies, biomedical implants (hip joint heads), diesel engine parts [1], and their use is increasing due to their enhanced mechanical properties and stability in different environments, especially at elevated temperatures.

Yttria (Y_2O_3) stabiliser is added to zirconia (ZrO_2) in order to retain high amounts of the desirable tetragonal phase form at room temperature avoiding undesirable phase transformations [2]. The yttria stabiliser is incorporated by the use of two different techniques, co-precipitation or coating. Most of the previous research at Sunderland University and elsewhere has involved the use of coated starting zirconia powders with 2.5–3 mol% yttria, but now the emphasis is on co-precipitated 3 mol% yttria materials because of their higher purity which enables more precise control of properties during manufacturing and their greater availability in the market.

Yttria-stabilised zirconias have traditionally been manufactured by firing powder compacts in a temperature range of between 1400°C and 1450°C. However, there are limitations in the use of Y-TZP in many engineering applications, as desirable mechanical properties have been offset by poor resistance of the material to the effects of humid atmospheres, at temperatures of 60–500°C [2, 3], causing crystallographic phase instability and material deterioration. The resulting tetragonal to monoclinic phase transformation, accompanied by a small volume increase in the material of about 3–5%, induces stresses and can result in a loss of specimen integrity i.e., loss of the desirable properties of the material.

The relationship between microstructure and mechanical properties in Y-TZP ceramics has been studied extensively in the past years. It has been found that Y-TZP ceramics, manufactured from co-precipitated starting powders, have high tensile strengths (1–2 GPa) and generally fracture toughnesses of 4–7 $MPa \cdot m^{1/2}$ favouring them for a large number of demanding structural applications [1, 4, 5]. Y-TZP ceramics manufactured from coated starting powders show higher fracture toughness values of about 8–15 $MPa \cdot m^{1/2}$ [4]. It has also been well established that these attractive mechanical properties are strongly influenced by grain size. For example, maximum strength is usually achieved with a small grain size ($<1\ \mu m$) whereas maximum toughness occurs at larger grain sizes ($\sim 2\ \mu m$) [6].

Swain and Becher [7, 8] having examined the grain size effect have shown that larger tetragonal zirconia grains in TZP ceramics have a greater propensity to undergo a stress induced phase transformation to the equilibrium monoclinic structure, resulting in an enhanced toughness. The mechanism involved is known as "transformation toughening."

Previous attempts to improve phase stability in moisture-bearing atmospheres have involved sintering at 1300°C–1400°C and the use of sintering aids, such as

transition metal oxides, in order to give enhanced densification at these lower temperatures and prevent the material degradation. Studies were carried out using a standard sintering heating and cooling rate of 10°C/min and 2 hrs holding time [4, 9, 10] with hydrothermal ageing in an autoclave at 180°C.

Noticeable improvements have been achieved, e.g., sintering a co-precipitated powder at 1200°C–1350°C produces a material that remains largely tetragonal for in excess of 7000 hrs [9] whereas for 1400°C sintering the material totally degrades in less than 20 hrs [9–11]. The reasons for these dramatic changes have not been clarified yet. One factor may be the grain size as increases have been found to be detrimental to ageing resistance [9]. Ramesh [10] observed that coated Y-TZP exhibited increased fracture toughness with a reduction in grain size resulting from low temperature sintering whilst the opposite effects were observed for co-precipitated powders. Inhomogeneous yttria distribution with a higher enrichment factor at grain boundaries for the coated powders enhances the ageing resistance compared to the co-precipitated powders where the distribution of yttria is homogeneous. Gill *et al*. [9] have also observed that for sintering in the region 1200°C–1350°C fracture toughness is not significantly affected by sintering temperature.

The role of beneficial dopants such as copper oxide (CuO) has also not been made clear, although such additions have been observed to result in higher densification and fine microstructures at lower sintering temperatures as well as enhancing mechanical properties such as fracture toughness and tensile strength [10]. Previous work at the University of Sunderland, by Gill *et al*. [10–12], indicates that the addition of copper oxide dopant to yttria-stabilised zirconia results in enhanced sinterability, finer grain sizes and higher fracture strengths. Lawson *et al*. [4], Ramesh [10] investigating the role of additives and in particular transition metal oxides indicate that their use can affect hydrothermal ageing resistance at lower temperatures below 1300°C and result in densification without grain growth. Low temperature degradation associated with the ageing-induced tetragonal to monoclinic phase transformation of TZP ceramics can be suppressed with low additions of CuO attributable in part to the small grain size developed in the body resulting from lower temperature sintering and to grain boundary modification due to the CuO dopant.

Burke *et al*. [3] analysing results for various zirconia powders, indicated that the presence of a glassy phase is beneficial in retarding hydrothermal degradation, with Tosoh TZ-3Y containing no detectable grain boundary glassy phase degrading at a higher rate. Segregation of yttria to the grain boundary also enhances degradation resistance [3]. Ramesh *et al*. [11], describe the presence of a liquid phase during the sintering of CuO doped samples, as a result of dissociation of CuO on heating at temperatures above 1100°C, forming molten Cu_2O (cuprous oxide) at the grain boundaries and the amount present is dependent on the CuO content in the starting powder. Seidensticker *et al*. [13] emphasise the low melting point of the CuO and the relatively large grain size observed in the CuO doped samples when compared to other doped systems, as being indicative of the mechanism responsible for the densification behaviour in CuO doped systems. The quantity of glassy phase, however, must have been very small since the grain boundary glassy phase and abnormal grain growth were not observed in the microstructure [13].

2. Experimental procedure

Samples in the form of round disks (pellets) have been manufactured from the following starting powders:

1. Plain Tosoh TZ-3Y co-precipitated powders.
2. Tosoh TZ-3Y co-precipitated powders doped with 0.05%wt of copper oxide.
3. Tosoh TZ-3Y, E' Grade, co-precipitated powders doped with 0.05%wt of copper oxide.

As a new supply of Tosoh TZ-3Y co-precipitated powder arrived to replenish stocks, there is a distinction between these two batches of powders used: (O) for the old powders and (N) for the new powders. Also it is necessary to mention the use of two different sizes of disk samples (19 mm Ø—3 g and 14 mm Ø—1.5 g), with reference 'b' or 'big disk' for the 19 mm diameter disks.

Samples were manufactured by using uniaxial cold die-pressing (35 MPa). Sintering was at 1300°C–1325°C, with constant ramp rates of 10°C/min, and holding times of 12 mins, 2 hrs and 4 hrs.

Surfaces were polished to a 1 μm finish. Densities were measured using a water immersion technique. Hardness values were obtained using the Vickers hardness method, which is also used as a tool for the evaluation of fracture toughness. From the Vickers indentation and the length of the cracks by using the equations derived by Niihara *et al*. [14] fracture toughness was measured. The materials were further characterised using optical and scanning electron microscopy (SEM). Phase analysis was carried out by x-ray diffraction (XRD).

Ageing studies were performed in superheated steam at 180°C using a mini-autoclave at 1 MPa internal pressure.

3. Review of results and discussion

A large number of tests has been carried out and the results have been analysed, with notable changes being observed after at least 72 hrs of ageing. The results are shown in Tables I and II and Figs 1–9.

Some general observations are:

(a) Enhanced densification by the addition of small quantities of CuO with the best results when doping is combined with longer holding times.
(b) Improved hardness for CuO doped samples.
(c) Longer holding times result in improved hardness for the CuO doped samples but the hardness values of the plain samples are lower than the ones sintered at shorter holding times.

TABLE I Measured properties of the samples

Sample	Density (Mgm^{-3})	Hardness Hv (GPa)	K_{1c} ($MPa \cdot m^{1/2}$)
1300°C-die-CuO(O) 2 hrs	5.99	12.7	4.59
1300°C-die-Plain-(N) 2 hrs	5.54	12.4	4.74
1300°C-die-Plain-(N) 4 hrs	5.77	10.5	4.80
1300°C-die-CuO(N) 4 hrs	6.08	13.7	4.60
1315°C-die-CuO(O) 12 mins (big disc)	5.93	13.1	4.43
1315°C-die-CuO(O) 12 min	6.06	13.2	4.40
1315°C-die-Plain-(O) 12 min	5.51	11.9	4.63
1315°C-die-CuO(N) 12 min	6.05	13.3	4.47
1315°C-die-Plain-(N) 12 min	5.48	12.2	4.71
1325°C-die-CuO(O) 12 mins (big disc)	5.93	13.4	4.49
1325°C-die-CuO(O) 12 min	6.08	13.3	4.42
1325°C-die-Plain-(O) 12 min	5.62	11.9	4.70
1325°C-die-CuO(N) 12 min	6.07	13.4	4.48
1325°C-die-Plain-(N) 12 min	5.57	12.2	4.77
1315°C-die-CuO(O) 2 hrs	6.09	13.4	4.49
1315°C-die-CuO(N) 2 hrs	6.10	14.2	4.69
1315°C-die-CuO(E) 2 hrs	6.06	14.1	4.45
1325°C-die-CuO(O) 2 hrs	6.02	13.4	4.89
1325°C-die-CuO(N) 2 hrs	6.08	13.4	4.92
1325°C-die-Plain-(N) 2 hrs	5.79	11.1	5.65

TABLE II Typical grain size measurements (μm). Since two different batches of Tosoh TZ-3Y powders were used there is a reference letter (O) for the old powder and (N) for the new powder

Plain Samples	Grain size (μm)	CuO-doped sample	Grain size (μm)
Tosoh TZ-3Y (N) 1300°C-2 hrs Die	0.17	Tosoh TZ-3Y (N) 1300°C-2 hrs Die CuO 0.05%	0.20
Tosoh TZ-3Y (N) 1300°C-4 hrs Die	0.16	Tosoh TZ-3Y (N) 1300°C-4 hrs Die CuO 0.05%	0.21
Tosoh TZ-3Y (O) 1315°C-12 mins Die	0.18	Tosoh TZ-3Y (O) 1315°C-12 mins Die CuO 0.05%	0.20
Tosoh TZ-3Y (O) 1325°C-12 mins Die	0.18	Tosoh TZ-3Y (O) 1325°C-12 mins Die CuO 0.05%	0.23

(d) Better fracture toughness for plain samples compared to the doped ones produced at the same temperature and same holding times.

(e) Longer holding times result in improved fracture toughness for both plain and CuO doped samples.

(f) Fracture toughness for CuO doped samples is not affected significantly by the holding time but by the sintering temperature.

(g) Fracture toughness values of co-precipitated samples are very low compared to the ones observed by previous research at the University of Sunderland when coated starting powders were used [9–12].

(h) CuO addition is more beneficial for the ageing resistance for the Tosoh TZ-3Y co-precipitated powders sintered for 12 minutes.

(i) Higher grain size values for the samples doped with CuO.

These results show some trends, which are different from those previously observed. A review of particular aspects of the results follows.

Plain co-precipitated samples have small grain sizes. The addition of copper-oxide (CuO) results in bigger grain sizes [4, 10–13]. The same effect could be achieved by increasing the sintering temperature.

Previous work at the University of Sunderland [11] with coated Tioxide samples indicated better ageing performance of the samples, sintered at lower temperatures, while sintering at higher temperatures produced samples which were susceptible to hydrothermal ageing and failure occurred in the early stages of the exposure.

Densification is also a key factor for the materials behaviour. Analysing the current results it has been observed that density can be improved by increasing the sintering temperature and by the addition of CuO Fig. 1. Longer holding times result in enhanced densification as well, Table I, Fig. 2. Samples doped with CuO showed enhanced densification at 1300°C sintered for 4 hrs instead of the standard 2 hrs. Higher values for density were obtained for CuO doped samples sintered at 1315°C for 2 hrs. An unexpected lower value for density was found for the sample doped with CuO, sintered at 1325°C for 2 hrs, Fig. 2. Densities increased as the sintering temperature increased for the doped samples. The addition of copper oxide reduced the sintering temperature required for achieving full densification for the samples. It has been observed that densities and grain-sizes of doped samples were equal to those of the plain materials sintered at much higher temperatures. Fired densities are related to grain size, as increasing one parameter increases the other one, too. Hayakawa *et al.* [15] attained full densification for CuO doped samples (0.2–0.7% mol) sintered at 1300°C for 2 hrs while for plain samples the required temperature to attain full densification was 1450°C.

Better fracture toughness values were obtained for plain samples compared to the doped ones produced at the same temperature and same holding times, Fig. 3. Sintering of plain samples at 1325°C for 2 hrs resulted in the highest value of K_{Ic} 5.65 $MPa \cdot m^{1/2}$ and this was the only sample exceeding 5 $MPa \cdot m^{1/2}$, but this was below the attractive values of 14 $MPa \cdot m^{1/2}$, obtained by previous researchers for coated Y-TZP powders.

Longer holding times resulted in improved fracture toughness for both plain and CuO doped samples, these being more noticeable for the samples sintered at 1325°C.

The fracture toughness for CuO doped samples was not affected significantly by the holding time but by the sintering temperature. Fracture toughness values of co-precipitated samples were very low compared to the ones observed by previous research at the University of Sunderland when coated staring powders were used [9–12].

Great emphasis has been given to the effects of grain size, as this parameter seems to control the properties of the Y-TZP [6–12]. Measured grain sizes have been tabulated in Table II, with the samples sintered at 1325°C, doped with CuO and sintered for 12 mins giving the highest grain size measurement of 0.23 μm.

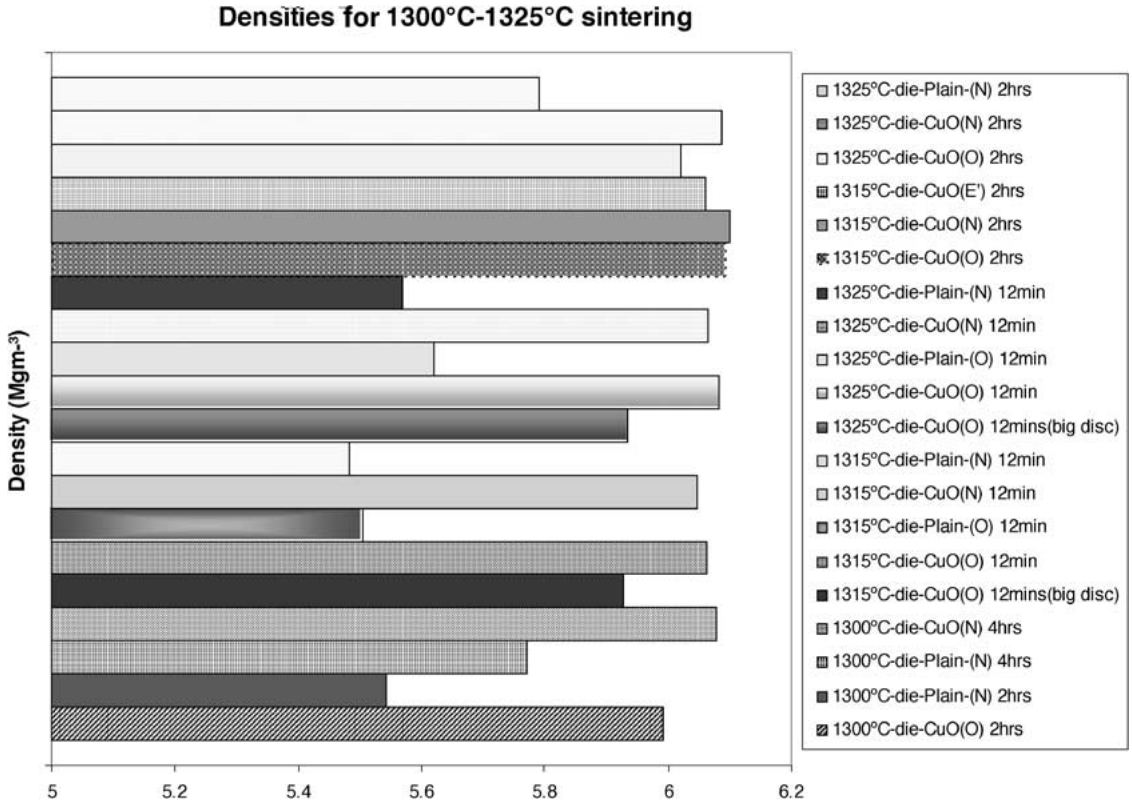

Figure 1 Fired densities of the samples.

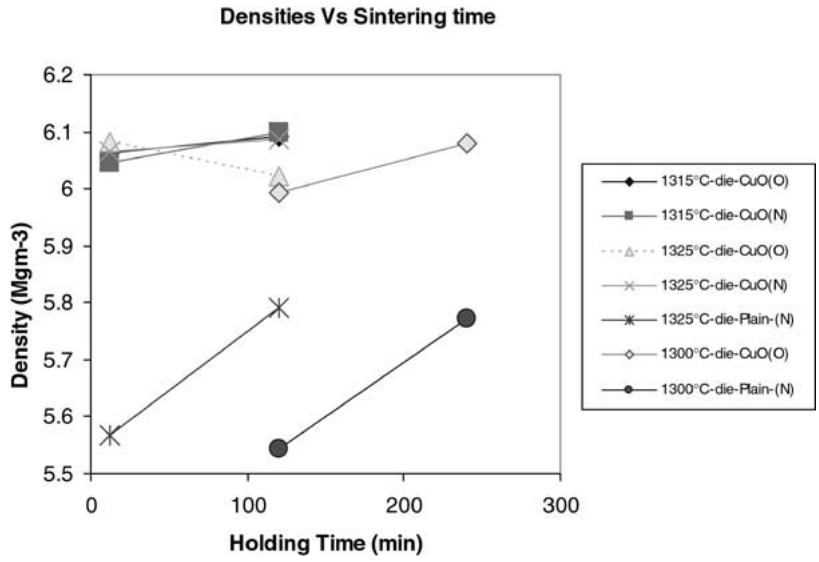

Figure 2 Effects of sintering time (holding time), on the densities of the samples.

Due to the effects of the grain size variation in different areas of the same samples and the measurement technique, the values shown are average values with a possible error of ±10%. The measurement was based on the line intercept analysis, technique introduced by Mendelson [16].

For the ageing resistance, CuO doped (19 mm dia.) samples manufactured from the old Tosoh powder, sintered at 1315°C and 1325°C performed better than the other samples with the outstanding 0.27% and 0.68% monoclinic phase contents respectively, after ageing for in excess of 5000 hrs. Reducing the holding time during sintering shows development in the ageing resistance of the plain samples with the best behaviour achieved by the samples manufactured from the new Tosoh powder, sintered at 1315°C for 12 mins, obtaining a 2% monoclinic phase content after 3000 hrs of ageing (Fig. 4).

Samples doped with CuO and sintered at 1325°C for 12 mins (14 mm dia.-small discs) developed more than 40% monoclinic phase content, after 76 hrs of ageing, maintaining the same amount for in excess of 3000 hrs, without any visible signs of degradation on the surface (Fig. 5). Similar behaviour was observed for the plain sample manufactured from the new Tosoh powder, sintered at 1325°C for 2 hrs (14 mm dia.-small disk) which developed more than 20% monoclinic phase content

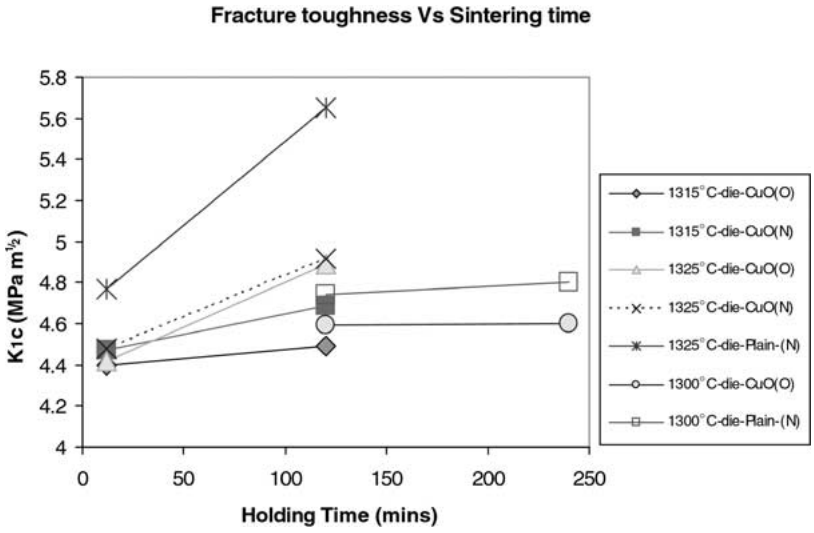

Figure 3 Effects of sintering time (holding time), on the fracture toughness of the samples.

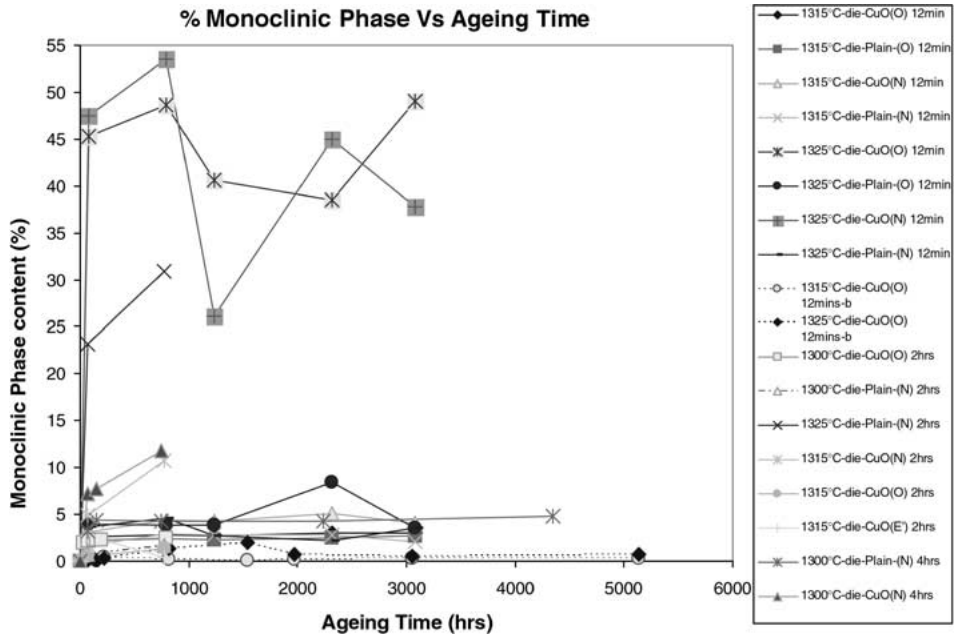

Figure 4 Ageing behaviour of the samples.

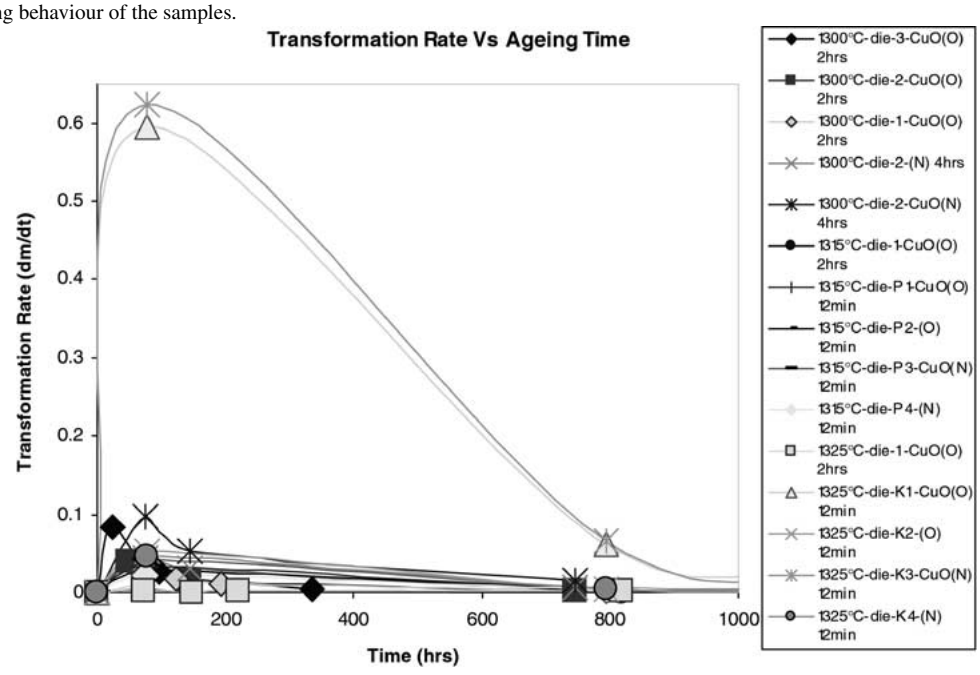

Figure 5 Tetragonal to monoclinic phase transformation rates (d*m*/d*t*).

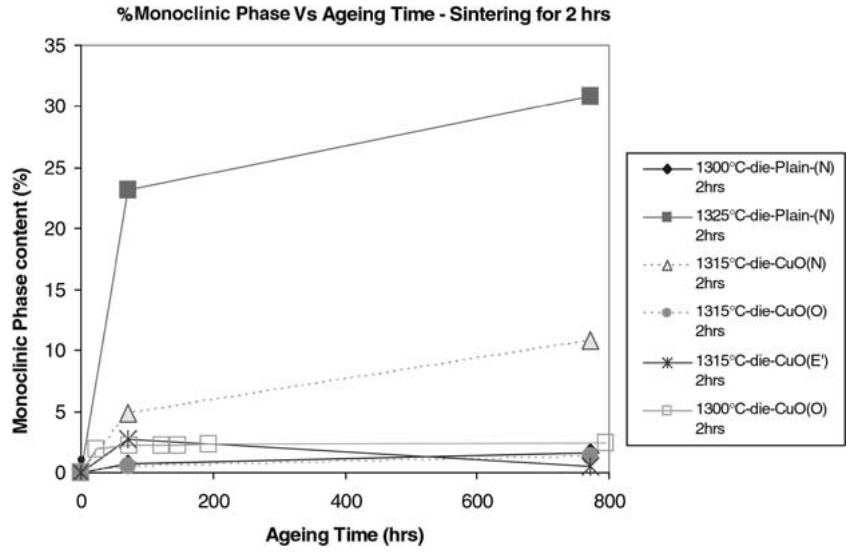

Figure 6 Ageing behaviour of the samples sintered for 2 hrs.

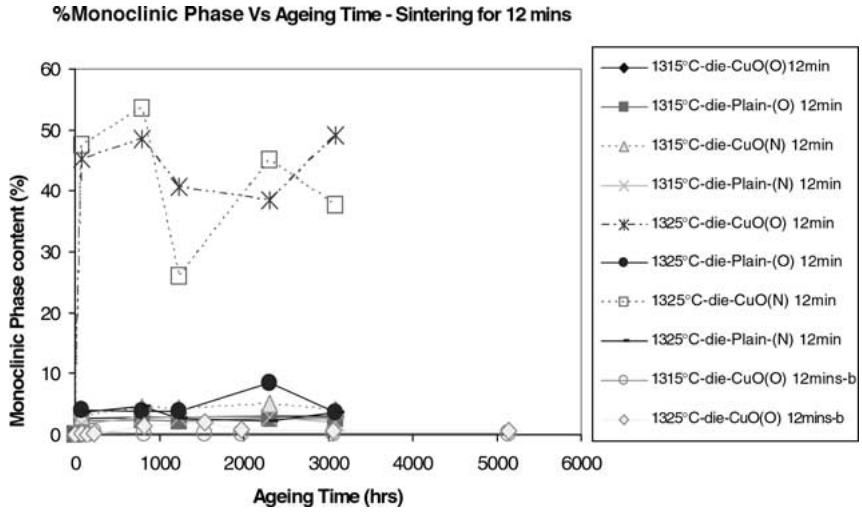

Figure 7 Ageing behaviour of the samples sintered for 12 mins.

after 72 hrs of ageing and about 30% after 750 hrs (Fig. 6). Samples showing such a big difference in behaviour are to be further tested and analysed in order to examine the poor ageing performance.

Transformation rates for samples sintered at 1300°C–1325°C are higher in the first 72–76 hrs of exposure in superheated steam at 180°C with the highest rate being found for the CuO doped samples sintered at 1325°C for 12 mins (Fig. 7). Samples doped with CuO and sintered for 4 hrs show better ageing behaviour than the ones sintered for 12 mins, for the first 750 hrs, Figs 4, 5. Plain samples sintered at 1300°C for 4 hrs show very good ageing resistance with less than 5% monoclinic content after 4000 hrs of ageing. Tosoh Grade E' samples doped with CuO, sintered at 1315°C for 2 hrs, have also shown good ageing resistance with less than 0.5% monoclinic content after 750 hrs of ageing. On Tosoh co-precipitated samples, in some cases, no marks of degradation were visible after 3000 hrs of ageing. Developments in the ageing resistance of the Y-TZP through doping with CuO, being generated from the current research, are shown in Figs 8, 9.

In Fig. 8 [17], data from the current experiments are presented in order to show the advances in the ageing resistance by the use of low quantities of CuO additive. It can be seen that plain samples at 1340°C and 1360°C also resist ageing with about 4% and 6% monoclinic content respectively.

Ramesh [18], reviewing the work undertaken by many researchers on the ageing behaviour of the Y-TZP points out that the ageing induced tetragonal to monoclinic phase transformation can be minimised or prevented by increasing the stabiliser content although this could overstabilise the tetragonal structure. In addition reducing the tetragonal grain size and modifying the grain boundaries by doping with sintering aids such as CuO, protects the grain boundary regions against hydroxyl reaction. In the same way an inhomogeneous yttria distribution in the zirconia structure, with higher yttria concentration near the grain boundaries, is also effective to prevent ageing.

Doping with CuO has proven to be beneficial for the ageing resistance of the lower temperature sintered samples. Further investigation is being carried out for the different performance of CuO doped samples at 1325°C. This investigation will include grain boundary analysis for those samples.

As grain size is related to the specimen processing conditions and the action of sintering additives, an attempt is being made to find the relationship between

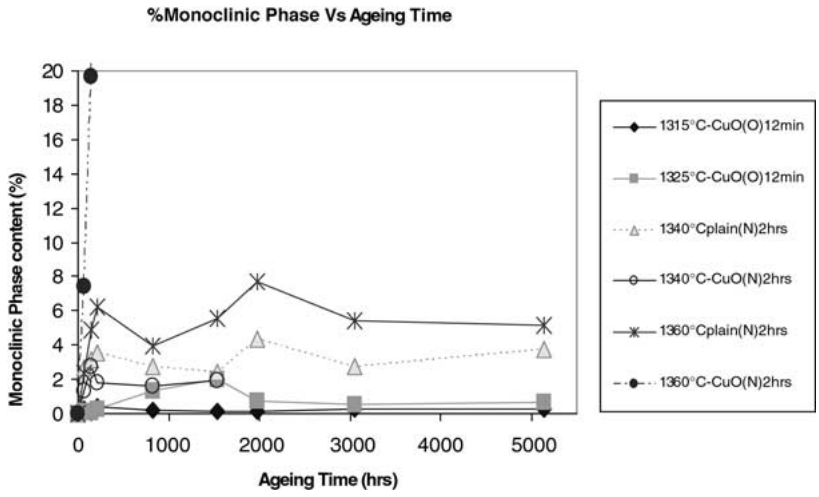

Figure 8 Long term ageing behaviour of the samples [17]. Samples disks are 19 mmØ.

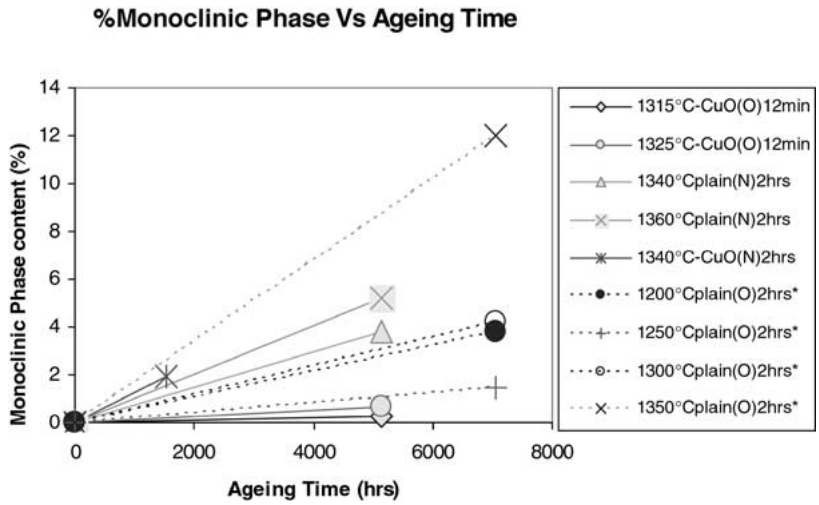

Figure 9 Ageing behaviour of the samples in excess of 5000 hrs [17]. * Denotes experimental data by Gill *et al*. [9].

monoclinic phase transformation rate during hydrothermal ageing and grain size, for the different manufacturing routes used. If such a relationship between monoclinic phase development and grain size exists, there must be a critical grain size after which phase instability occurs. However in the present work it is shown that change in ageing behaviour occurs for a very small variation of grain size. Results are being analysed to show whether such a huge change in ageing behaviour can occur for such a small grain size increase and if a grain size-density threshold factor is being involved.

4. Conclusion

After performing a large number of tests for the Y-TZP samples, the results obtained have been analysed to show the following overall effects:

1. Shorter holding times produce materials which resist hydrothermal ageing better than the ones produced at longer holding times. Better ageing resistance was observed for CuO doped samples sintered at 1315°C with 12 mins holding times and for plain samples sintered at 1300°C with 2 hrs holding times.

2. Combinations of longer holding times with CuO addition, have proven to be detrimental for the ageing resistance of the samples, regardless of the enhanced densification.

3. Enhanced densification and increased grain sizes were obtained by the addition of small quantities of CuO.

4. Improved hardness values were measured for CuO doped samples.

5. Plain samples had higher fracture toughnesses than the doped samples at the same sintering temperatures and holding times.

It can be said that doping with small quantities CuO at 1315°C, sintering for 12 minutes, has proven to be beneficial for the ageing resistance of co-precipitated Y-TZP samples, despite the fact that fracture toughness values were lower than those of the plain samples. Since there was abnormal behaviour in ageing of samples doped with CuO and sintered at 1325°C for 12 minutes, further testing is to be carried out and also TEM examination in order to investigate the cause of such a huge difference in material's performance.

Further work includes doping of samples with CuO and reducing the holding times to 12 mins-1 hr in order to evaluate the benefits of the oxide doping at lower sintering temperatures. Also doping of pure TZ-0 zirconia powders with yttria using the coated powder technique

will be involved in the current investigation in order to examine the effects of the powder preparation methods on the ageing resistance of the Y-TZP material.

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