

LOW-TEMPERATURE DEGRADATION (LTD) BEHAVIOUR OF CUO-DOPED TETRAGONAL ZIRCONIA CERAMIC

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Submitted September 5, 2011; accepted December 29, 2011

Keywords: Y-TZP, Zirconia, Low-Temperature Degradation, Corrosion, Phase Transformation

In the present work, the low-temperature degradation (LTD) behavior of undoped and copper oxide (CuO) doped yttria-tetragonal zirconia polycrystals ceramics sintered at 1300°C was investigated. The zirconia samples were tested in three different media i.e. superheated steam at 180°C/10 bar; refluxing conditions in 20% hydrochloric solution at 110°C and in hot air at 180°C to determine the effect of hydroxyl content in triggering the tetragonal to monoclinic phase transformation. The study found that the additions of CuO significantly reduced the rate of LTD phase transformation in all media tested. The undoped zirconia exhibited severe LTD when exposed to media containing 100% hydroxyl content. Although the CuO-doped samples were generally found to have better LTD characteristics, cross-sections of aged specimens (after 200 hours of exposure in superheated steam) revealed that very thin measurable monoclinic layers were developed. The presence of hydroxyl in the test media was found to have played a significant role in controlling the LTD of zirconia ceramics.

INTRODUCTION

Yttria-tetragonal zirconia polycrystal ceramics are characterised by exceptionally high strength, enhanced fracture toughness and good wear resistance [1-3]. These property improvements have been attributed to the stress-induced phase transformation from metastable tetragonal zirconia (t) to the monoclinic (m) form, the mechanism of which is subsequently known as transformation toughening [4]. As a result zirconia has been employed for a host of engineering components, including clinical applications [4,5].

However, one of the major barriers to the widespread use of Y-TZP ceramics is the low-temperature degradation (LTD) phenomenon or ageing, in particular at temperatures ranging from 60°C to 500°C and in the presence of moisture [6,7]. This premature ageing-induced (t) to (m) phase transformation and the accompanying microcracking which was for the first time reported by Kobayashi et al. [8], and ever since has been widely studied [9,10]. Although the experimental observations of the ageing phenomenon are well understood, the actual mechanism responsible for the degradation has not been unequivocally explained [7, 11-13].

In general the experimental observations on LTD can be summarised as follows [7, 14-20]:

1. The degradation proceeds most rapidly at temperatures of 150°C-300°C and the degree of deterioration is dependent on ageing time, environment and the presence of hydrostatic pressure [7, 14].
2. The degradation is as a result of (t) to (m) phase transformation and when the monoclinic content or layer depth exceeds a certain limit, microcracking will occur with a subsequent deterioration in the mechanical properties. In extreme cases, total structure destruction within 24 hours has been observed [15, 16].
3. The transformation usually starts at the free surface and progresses inward with time [17, 18].
4. Water which can be present in the form of liquid, vapour or in other solutions has been identified as the catalyst of the phase transformation [16].
5. Two of the well known tactics frequently employed in suppressing the degradation are the increase in stabiliser content and the decrease in grain size of the sintered microstructure [19, 20].

It has been reported that the ageing-induced (t) to (m) phase transformation could improve toughness in

some Y-TZPs by creating a compressive stress layer near the free surface [21]. However, this beneficial effect is expected to diminish with increasing transformation depth since the development of microcracks would act as fracture origins, thus decreasing strength.

Some of the most important parameters governing the tetragonal phase stability during ageing are powder manufacturing technique, impurity content, the presence of certain dopants, sintered microstructure such as grain size, yttria content and distribution and grain boundary phase. Often alteration in one feature brings changes to the other, hence affecting the LTD behaviour. For instance, increasing the yttria content would tend to over-stabilise the tetragonal phase, thus retarding ageing, but this would have a negative effect on transformation toughening. Therefore strict control should be exercised in order to achieve optimum conditions in terms of densification, mechanical properties and LTD resistance.

In this respect, the use of sintering additives, in particular transition metal oxides such as CuO, have been found to aid densification at relatively low temperatures, to improve mechanical properties, to suppress grain growth and to enhance ageing resistance in Y-TZP ceramics [22,23]. It has also been found that the powder manufacturing method for incorporating yttria i.e. co-precipitation or coating technique, which determines the distribution of yttria in the grains i.e. homogeneous or inhomogeneous distribution, has an effect on the ageing resistance of Y-TZPs [23,24].

The aims of the present work were to study the effects of using CuO as a sintering aid in Y-TZP ceramics on the LTD behavior during exposure in hostile environments.

EXPERIMENTAL

The starting Y-TZP powder containing 2.5 mol% of yttria was obtained from Tioxide Specialties Ltd., UK. The as-received zirconia powder had a total impurity concentration of about 1.7 wt%, with 0.08 wt% aluminum oxide and 1.6 wt% hafnium oxide as the major impurities. Varying amounts of high purity copper (II) oxide, CuO i.e. 0.05, 0.1 and 0.2 wt% were attrition-milled with the undoped zirconia powder using distilled water as the milling media and 1 mm diameter Y-TZP milling balls. For each doped samples the milling parameters were kept constant, i.e. at a milling speed of ~1960 rpm and for half an hour prior to filtration. In a typical set-up, the slurry was filtered 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. Finally, the soft dried powder cake was crushed and sieved to obtain ready-to-press CuO-doped Y-TZP powders. Disc samples (20 mm in diameter) were prepared by uniaxial pressing followed by cold isostatic pressing at 200 MPa. All the samples

were pressureless sintered in air atmosphere for 2 hours at 1300°C using a ramp rate of 10°C/min. The sintered samples were subsequently ground and polished on one face to a 1 µm surface finish prior to testing.

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-Kα as the radiation source. The fraction of surface monoclinic content was evaluated using the method of Toraya et al. [25]. The microhardness (*H*) were measured on polished samples using the Vicker's indentation method at a constant load of 50 kg. 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 [26]. The hydro-thermal ageing was performed in an autoclave containing superheated water at 180°C and 10 bar for up to 200 h. The acidic corrosion was under refluxing conditions in 20% hydrochloric acid (HCl) at 110°C. Samples were also exposed in hot air at 180°C for periods ranging up to 200 h. The low-temperature degradation was assessed by monitoring changes in surface monoclinic content and changes in bulk density. For the latter test, the aged samples were dried in an oven at 100°C for 2 hours prior to measurement using the water immersion method. In addition, all the aged samples in superheated steam were sectioned to measure the transformed monoclinic layer depth by using an optical microscope.

RESULTS AND DISCUSSION

The as-sintered properties of the undoped and CuO-doped Y-TZP ceramics are given in Table 1. In the present work, 1300°C was chosen as the sintering temperature for all samples because this was identified as the optimum temperature for the CuO-doped Y-TZP and to restrict the variations in the grain sizes of all the samples. All sintered samples exhibited the tetragonal structure after sintering. The grinding and polishing of the sintered samples did not alter the tetragonal phase content in the sintered samples. In general, the results showed that CuO was effective in enhancing the densification of the zirconia ceramic.

Table 1. The as-sintered properties of undoped and CuO-doped zirconia.

CuO content	Bulk density (Mgm ⁻³)	<i>H</i> (GPa)	Average grain size (µm)
Undoped	5.91	10	0.16
0.05 wt%	6.03	11	0.13
0.10 wt%	6.03	11	0.14
0.20 wt%	6.03	11	0.15

The effect of superheated steam at 180°C and 10 bar on the tetragonal (t) to monoclinic (m) phase transformation of the zirconia samples is shown in Figure 1. The undoped Y-TZP exhibited poor resistance to LTD when compared to the 0.05 wt% CuO-doped sample. The devastating effect of LTD on the structure of the undoped zirconia can be visible through the formation of severe microcracks within the body of the sample as typically shown in Figure 2. The results presented in Figure 1 also indicated that the ageing-induced (t) to (m) phase transformation proceeded at different rates for the CuO-doped samples. The 0.05 wt% CuO-doped samples exhibited the best LTD resistance in superheated steam i.e. developing less than 40% monoclinic content after 200 h of exposure. On the contrary, the 0.1 wt% CuO dopant sample exhibited reasonably good resistance during the early stages of exposure (< 50h) compared to the undoped Y-TZP. The 0.2 wt% CuO-doped sample exhibited lower initial LTD kinetics when compared to the undoped Y-TZP ceramic during the first 24 h of exposure, however both the samples attained monoclinic saturation levels at about the same period of exposure.

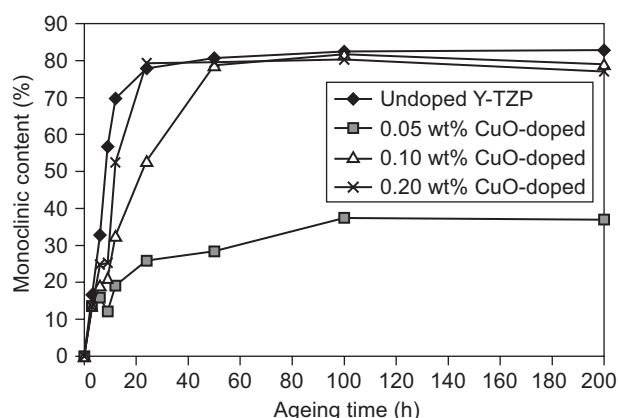


Figure 1. The effects of CuO additions on the hydrothermal ageing behaviour (180°C and 10 bar) in zirconia.

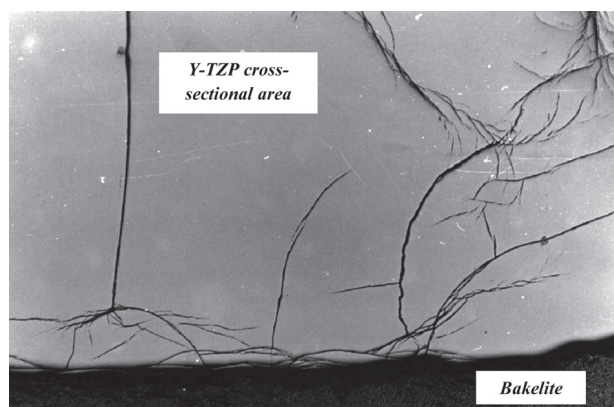


Figure 2. Optical micrograph of a polished cross-section area of undoped zirconia revealing severe microcracking resulting from monoclinic phase formation after exposure for 24 h in superheated steam at 180°C and 10 bar.

All the CuO-doped samples were intact after 200 hour of exposure, unlike the undoped samples which has degraded significantly and suffered a drastic drop in bulk density with ageing time as shown in Figure 3. The 0.05 wt% CuO-doped sample showed no sign of surface spalling although it has developed about 37% monoclinic content (Figure 1) in the zirconia matrix.

The increase in monoclinic phase content with increasing CuO content was expected. It has been postulated previously [23,24] that the reduction in yttria enrichment at grain boundary regions in the zirconia structure as a result of increasing yttria dissolution into the CuO-rich phase due to increasing CuO contents would have lowered grain boundary resistance of the ceramic to water attack. However, small amounts of yttria dissolution as in the case of 0.05 wt% CuO additions was beneficial for grain boundary modification and this is manifested in the LTD resistance of the ceramic as depicted in Figure 1.

The effect of refluxing in 20% hydrochloric acid at 110°C on the monoclinic phase development with time is shown in Figure 4. The undoped ceramic aged

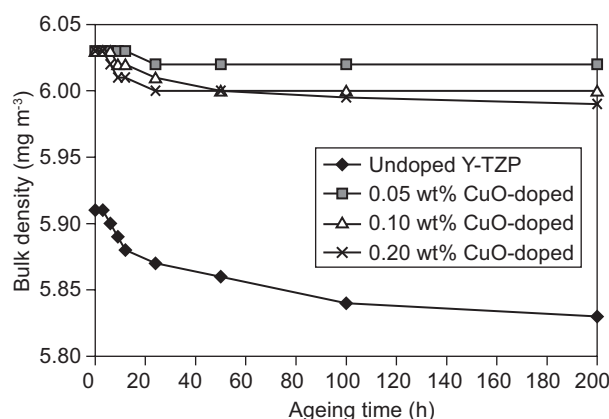


Figure 3. The effect of superheated steam on the variation in bulk density of zirconia samples.

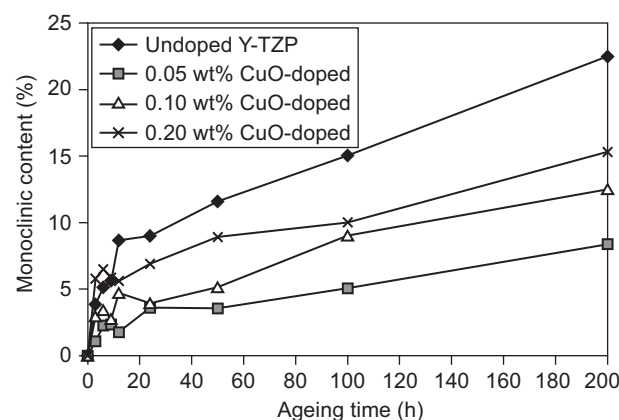


Figure 4. The surface monoclinic phase development in Y-TZPs after refluxing in 20% HCl solutions at 110°C.

rapidly within the first 12 hours of exposure and then proceeded steadily with time as shown in Figure 4. On the other hand, the 0.05 wt% CuO-doped samples once again exhibited better resistance to LTD and developed less than 7% monoclinic content after 200 h of exposure.

It is believed that the poor corrosion resistance of the zirconia was mainly due to attack near grain boundary regions resulting in destabilisation of the tetragonal phase thereby inducing the phase transformation to the monoclinic symmetry in the zirconia structure. Since it has been reported [23] 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 LTD process. The fact that the undoped sample (which is expected to have higher intragranular yttria gradient) exhibited the poorest corrosion resistant supports this view. The possibility has not been excluded that during LTD, the hydroxyl groups from the media could react with Y_2O_3 along grain boundary regions to form Y-OH bonds. Thus, the presence of a CuO- Y_2O_3 phase at grain boundary regions would prevent the OH reaction with Y, therefore enhancing corrosion resistance.

The effects of exposure in hot air at 180°C on the tetragonal phase stability in Y-TZP are shown in Figure 5. The transformation from tetragonal to monoclinic symmetry 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 [24] developed a high monoclinic content, viz. > 50% after exposure for 200 h. In contrast, the CuO-doped ceramics exhibited better resistance to phase transformation. In particular, samples containing 0.05 wt% CuO exhibited the least phase transformation i.e. developing less than 4% monoclinic phase after 200 h. Similar observations were also noted for the 0.1 wt% CuO-doped samples which had developed less than 6 % (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 almost constant after 3 h, developing about 12% monoclinic content after 200 h.

Selected samples exposed in superheated steam conditions were sectioned at each exposure time interval to evaluate the monoclinic layer thickness developed in the material. The monoclinic layer thickness measurements revealed that all the CuO-doped samples had very thin monoclinic layers which developed after 50 h of ageing as given in Table 2. The addition of 0.05 wt% CuO was most effective in retarding the monoclinic layer propagation rate as depicted by the very thin layer developed ($\sim 4 \mu\text{m}$) if compared to $\sim 750 \mu\text{m}$ thickness for the undoped ceramic.

Table 2. Monoclinic layer thickness of Y-TZPs exposed for different intervals in superheated steam conditions.

CuO content	Monoclinic layer thickness (μm)				
	3 h	24 h	50 h	100 h	200 h
Undoped	6	80	160	350	750
0.05 wt%	—	—	1	3	4
0.10 wt%	—	—	8	20	40
0.20 wt%	—	—	23	40	70

The effect of hydroxyl content on the LTD kinetics and severity of the phase transformation in the zirconia matrix could be visible by comparing the LTD of the undoped ceramic as shown in Figure 6. The results indicated that the hydroxyl content in the test media does play a part in the degradation process. Other variables that cannot be excluded are the applied pressure (as in the case of superheated steam) and the test temperature, which could have played a contributing role in the LTD process. Further work is in progress to study the relationship between the test parameters and their contributing role in the LTD process.

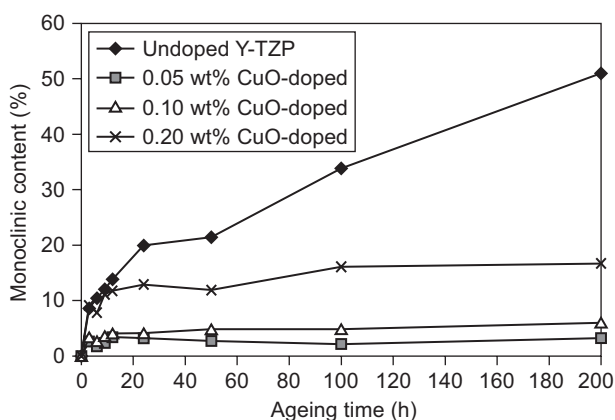


Figure 5. The effects of ageing in hot air at 180°C on the monoclinic phase development in Y-TZPs.

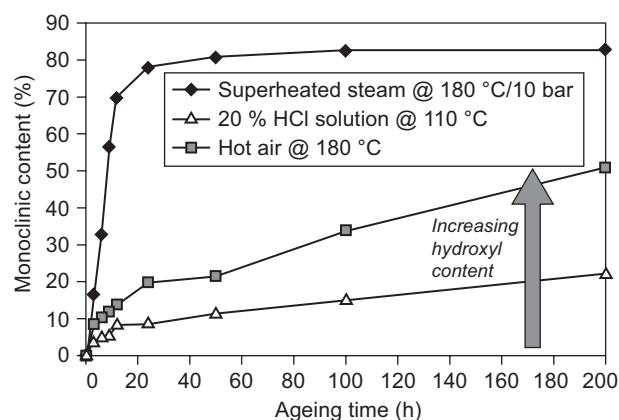


Figure 6. Effect of hydroxyl content in the test media on the LTD kinetics of undoped Y-TZP.

CONCLUSIONS

The additions of small amounts of CuO (up to 0.2 wt%) to Y-TZP were found to be beneficial as a sintering aid in Y-TZP ceramics. The bulk densities of all the doped samples were generally higher ($> 6 \text{ Mgm}^{-3}$) than for the undoped ceramics when sintered at 1300°C . The LTD phenomenon of Y-TZP ceramics as a result of tetragonal to monoclinic phase transformation was suppressed via the additions of CuO dopant. Studies conducted in three different environments containing different levels of hydroxyl contents showed that the addition of 0.05 wt% CuO was most effective in retarding the LTD phase transformation in such hostile environments. The undoped zirconia exhibited severe LTD when exposed in superheated steam conditions as compared in 20% HCl solution. For all the samples tested, the severity of degradation increases when exposed in the test media in the following order: hot air at 180°C , refluxing conditions in 20% HCl solution at 110°C and superheated steam at $180^\circ\text{C}/10 \text{ bar}$. Dissolution of yttria near grain boundary regions as a result of hydroxyl reaction was believed to be responsible for triggering the monoclinic nucleation in the zirconia structure.

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