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The effects of copper and iron oxide additions on the sintering and properties of Y-TZP

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Yttria-tetragonal zirconia polycrystals (Y-TZP) with a range of yttria contents were prepared from powders neutralized during processing with ammonium hydroxide and sintered at temperatures of 1300–1700 °C. Iron or copper oxide was added and studies made of body characteristics, mechanical properties and ageing resistance. Densification was aided by higher yttria concentrations. The effects of the oxide additives were dependent on amounts present and sintering conditions, including ramp rates and holding temperatures. Ageing resistance was significantly improved for both oxide additions fired to lower temperatures but rapid transformation to monoclinic phase was observed for materials with larger grain sizes associated with higher sintering temperatures.

1. Introduction

Yttria-tetragonal zirconia polycrystals (Y-TZP) have good mechanical properties such as bend strength and fracture toughness, and these are associated with the tetragonal to monoclinic phase transformation which occurs ahead of propagating crack fronts.

There is evidence that the addition of transition metal oxides to the Y-TZP powder improves sintering behaviour, with higher densities being attainable at lower temperatures [1–3]. The effects of these additives on properties have not been clearly established.

It is well-known that Y-TZP materials are susceptible to various environments, e.g. water/water vapour, and with maximum kinetics occurring at 100–300 °C resulting in poor resistance to ageing. The loss of mechanical properties during ageing is associated with the tetragonal to monoclinic transformation occurring from the surface into the interior of components [4]. The rate of this transformation is one of the most important factors in the ageing process. In addition, the depth of monoclinic phase present for a given ageing time increases linearly with time [3, 5] and is dependent upon the grain size and stabilizer content [6].

Transition metal oxide additions to Y-TZP are likely to have an effect on ageing resistance if they influence densification, result in lower grain sizes and are to be found associated with grain boundaries. Yttria content, impurity level and method of powder preparation, e.g. co-precipitation, co-coating or mixing, are all factors which will affect resistance to degradation.

The various mechanisms of ageing previously proposed [7–10] have involved several processes for chemical and mechanical degradation. Most frequently it has been suggested that OH^- ions are adsorbed at the Y-TZP surface leading to the formation of Zr–OH or Y–OH groups which form at stressed sites. Further migration of OH^- into the structure creates stresses leading to transformation [8].

The present work was concerned with the investigation of the effects of: (i) yttria levels, nominally 2, 2.5, 3 and 4 mol %; (ii) type of neutralizing solution used during powder preparation, e.g. NH_4OH or NaOH; (iii) sintering temperatures and ceramic body characteristics; (iv) dopants, a range of levels of oxides of iron and copper, and their effects on forming characteristics and properties including ageing resistance; and (v) sintering temperature and ageing behaviour.

2. Experimental procedure

The method used in the production of the powders is described elsewhere [11]. Neutralization during this preparation was with either ammonium hydroxide or caustic soda. The transition metal oxides were added to the zirconia using a coating technique. Pellets were die pressed at 10 MPa and then isostatically pressed at 200 MPa. Sintering was at temperatures between 1300 and 1700° C with ramp rates in the range 2.5–15° C min^{-1}.

The starting powders and the fired test pieces were characterized where appropriate to determine particle size, specific surface areas, grain size, phase content and mechanical properties. Some samples were aged in an autoclave at 180° C in superheated water at a steam pressure of ~ 10 bar (~ 1 MPa).

3. Results and discussion

3.1. Particle size

Powders were in the nanometre range with particle sizes measured by transmission electron microscopy (TEM) of 0.07–0.08 μm. Specific surface areas (SSA) determined by the BET method for powders containing between 2 and 4 mol % yttria prepared by ammonium hydroxide or caustic soda neutralization, were between 19 m^2g^{-1} (2.5 mol % yttria, NaOH) and 30 m^2g^{-1} (4.0 mol % yttria, NaOH). For given yttria concentrations, ammonium hydroxide-neutralized powders had higher SSA values by about 2 m^2g^{-1} than for caustic soda powders, except for 2.0 mol % yttria materials.

3.2. X-ray diffraction

For powders with 2–4 mol % yttria prepared with both neutralizers, the monoclinic content varied from 90%–95%.

Pellets sintered at 1400° C showed tetragonal phase contents of 79%–98%, the lower value being for the 2 mol % yttria pellets; see Table I which contains data for ammonia-neutralized material. For 2.5 mol % yttria, the tetragonal content had increased to 98%. There was a slightly increasing amount of cubic phase present for the 3 and 4 mol % yttria batches.

TABLE I Composition, phase content and density of Y-TZPs

Yttria content (mol %)	Powder monoclinic content (%)	Sintered tetragonal content (%)	Pellet density ($Mg\,m^{-3}$)
2.0	90.4	79.0	5.85
2.5	93.4	97.8	5.96
3.0	94.0	97.8	6.01
4.0	94.1	97.9	6.07

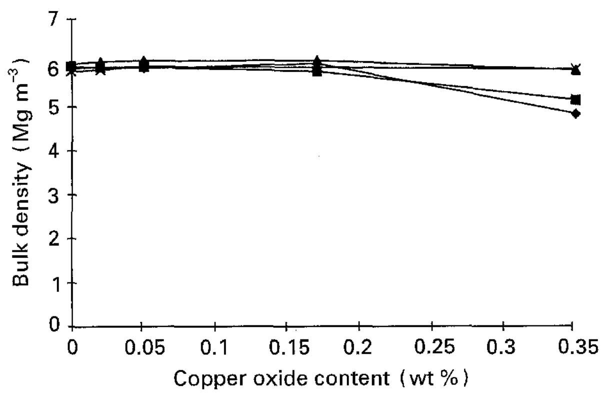

Figure 1 The effect of ramp rate on the sintered density of Y-TZP with respect to dopant concentration: (◆) 2.5, (■) 5, (▲) 10 and (×) 15 °C min^{-1}.

3.3. Density

As yttria content increased, densities rose from 5.85 $Mg\,m^{-3}$ to 6.07 $Mg\,m^{-3}$, the lower values being associated with higher amounts of monoclinic phase, i.e. where there is less tetragonal-phase stabilization, see Table I.

For CuO dopant levels of 0.02–0.17 wt %, higher densities were measured for lower ramp rates ($< 15°$ C min^{-1}) and low holding times, see Fig.1. The 0.35 wt % CuO samples gave high densities, (> 5.94 $Mg\,m^{-3}$), for high ramp rates (15° C min^{-1}) and 5 h holding times. Similar results were obtained for up to 0.5 wt % Fe_2O_3 additions.

3.4. Grain size

For 1300 and 1700° C sintering temperatures, the influence of copper and iron oxide contents on grain size in 2.5 mol % yttria pellets are shown in Table II. Consequently, some increase in grain size resulted from the addition of transition metal oxides particularly at the higher sintering temperature. However, the improved sinterability was associated with a decrease in the tetragonal content and a concomitant increase in the amount of monoclinic and/or cubic phase present.

3.5. Hardness

For up to 0.17 wt % CuO additions there was little increase in hardness with values around 12–13 GPa. For 0.35 wt % CuO specimens, hardnesses were between 4 and 11 GPa for sintering ramp rates up to 1400° C of 2.5–15° C min^{-1}, respectively, see Fig. 2. For up to 0.17 wt % CuO, slightly higher hardnesses were measured for 5° C min^{-1} samples. For 0–0.17 wt % CuO, maximum hardnesses were observed at a soak time of 120 min, Fig. 3.

The effects on hardness were associated with grain size and/or the decrease in the tetragonal phase. This was particularly striking in the 0.35 wt % copper oxide pellets with lower tetragonal-phase samples having lower hardnesses.

TABLE II Grain size, composition and sintering temperature for doped Y-TZPs

Sintered at 1300° C			Sintered at 1700° C		
Composition (wt %)	Grain size (μm)	Tetragonal content (%)	Composition (wt %)	Grain size (μm)	Tetragonal content (%)
0.00 CuO	0.29	98	0.00 CuO	1.49	100
0.07 CuO	0.58	99	0.05 CuO	2.60	100
0.25 Fe_2O_3	0.33	94	0.25 Fe_2O_3	3.12	50
			0.50 Fe_2O_3	3.60	51

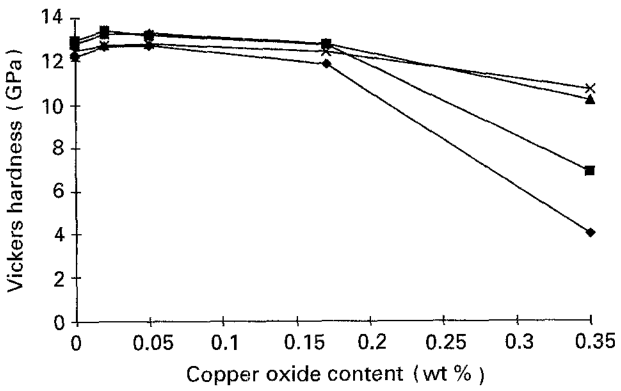

Figure 2 The effect of ramp rate on the Vickers hardness of Y-TZP with respect to dopant concentration: For key, see Fig. 1.

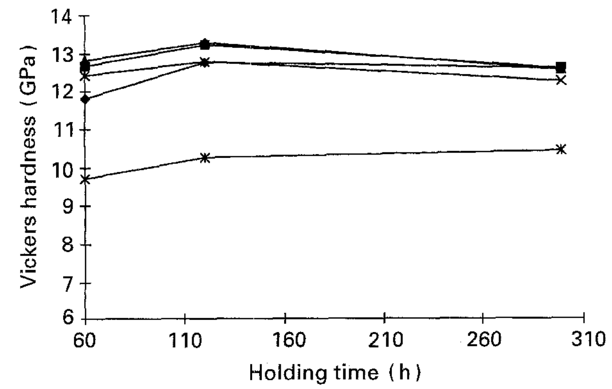

Figure 3 The effect of dopant concentration on the Vickers hardness of Y-TZP with respect to holding time: (◆) 0, (■) 0.02, (▲) 0.05, (×) 0.17, (∗) 0.35.

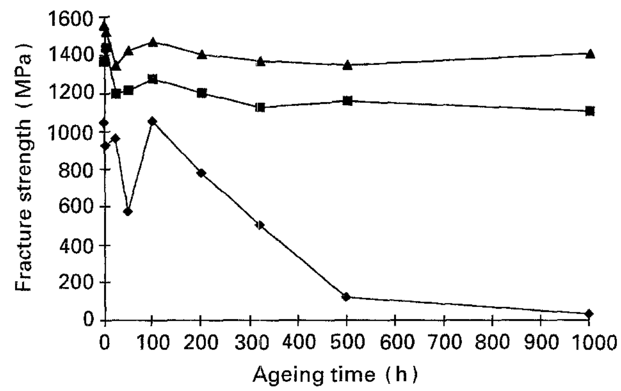

Figure 4 The effect of sintering aids on the fracture strength of Y-TZP with respect to ageing time: (◆) undoped Y-TZP, (■) + 0.07 wt % CuO, (▲) + 0.25 wt % Fe_2O_3.

3.6. Strength

Strengths were measured in a biaxial disc flexure method [12] and ranged from 1049–1558 MPa as additive content was increased from zero to 0.25 wt % iron oxide. For several samples containing CuO and Fe_2O_3, there were impressive ageing characteristics with, in some cases, high strength retention, even after 1000 h at 180° C in autoclave conditions, see Fig. 4. The samples with the best strength retention were those with low surface monoclinic content, Fig. 5. The best ageing resistances were obtained with 0.25 wt % Fe_2O_3 and 0.07 wt % CuO.

Higher strengths and better resistance to ageing degradation are attributable to higher densities resulting from improved sinterability, and to yttria enrichment at the grain boundaries [3, 13].

3.7. Fracture toughness

The maximum values of fracture toughness were measured for sintering holding times of 120 min, Fig. 6. In general, increasing copper oxide content gave lower K_{Ic} values, with the 0.35 wt % CuO specimens having particularly low values of ~ 4.5 MPa $m^{1/2}$ as compared with the highest values of 13 MPa $m^{1/2}$.

3.8. Ageing behaviour and sintering temperature

A comparison was made between the ageing behaviour of plain Y-TZP and Y-TZP doped with 0.25 wt % Fe_2O_3 sintered at 1300 and 1700° C. The iron oxide-bearing samples endured at least 1000 h (sintered at 1300° C) without much strength reduction and even the plain Y-TZP had some strength after 1000 h.

The 1700° C samples degraded rapidly during ageing and, in this case, the 0.25 wt % iron oxide material crumbled almost immediately; see Fig. 7 which shows the percentage of monoclinic phase versus ageing

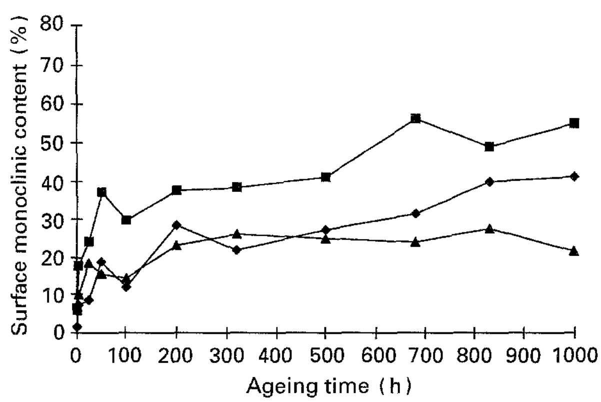

Figure 5 The effect of sintering aids on the surface monoclinic content of Y-TZP with respect to ageing time (sintered at 1300 °C). For key, see Fig. 4.

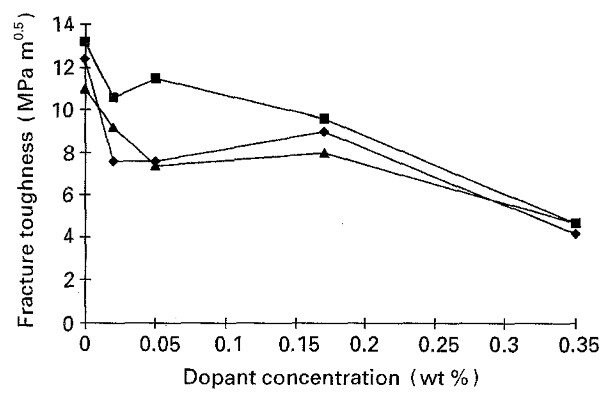

Figure 6 The effect of holding time on indentation fracture toughness of Y-TZP with respect to dopant concentration: (◆) 60, (■) 120 and (▲) 300 min.

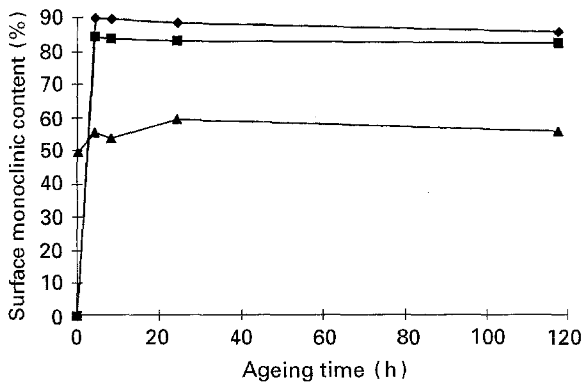

Figure 7 The effect of sintering aids on the surface monoclinic content of Y-TZP with respect to ageing time (sintered at 1700 °C): (◆) undoped Y-TZP, (■) + 0.05 wt % CuO, (▲) + 0.25 wt % Fe_2O_3.

time. The poor ageing behaviour was accompanied by dramatic increases in the amounts of surface monoclinic phase present.

The rapid degradation was almost certainly exacerbated by the presence of large grains from the high sintering temperature and the action of the transition metal oxides.

4. Sintering aids and their influence on properties

The effects of transition metal oxide additives were complicated depending on the amount present, the ramp rate and the sintering temperature. The action of both copper and iron oxides is believed to be via transient liquid phases, although physical evidence for this is still being sought. In superplastic zirconia ceramics containing copper oxide dopants, a liquid phase has been identified [14]. However, TEM studies on copper oxide-doped coated Y-TZPs have shown that there is no evidence of intergranular glassy phases being present [3] at room temperature. Copper oxide melts at a lower temperature than iron oxide, so the former is more effective at lower temperatures. These additives improve densification with greater effect at higher concentrations. Longer times at higher temperatures and for greater dopant levels are likely to lead to grain growth and reduced mechanical properties. The measurements of grain size and phase content supply some confirmatory evidence for these theories.

5. Conclusions

1. Small differences in powder characteristics and sintered phase contents were found for the two neutralization methods.

2. Increased densities were obtained for higher yttria concentrations. The effects of differences in ramp rates during sintering depend on the dopant level.

3. Copper and iron oxides promote grain growth in Y-TZP particularly at higher sintering temperatures.

4. Additions of copper oxide improve the hardness of Y-TZP over various ramp rates and holding times, maximum values being obtained for 1300° C, $10°\,C\,min^{-1}$ and a soak time of 120 min.

5. Metal oxide additions have a beneficial effect on the ageing resistance of Y-TZP, particularly for lower sintering temperatures.

6. Fracture toughness values are adversely affected by additions of copper oxide to Y-TZP.

7. Ageing resistance is severely lessened with increasing grain size resulting from high sintering temperatures.

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References

1. N. KIMURA, S. ABE, Y. HAYASHI, J. MORISHITA and H. OKAMURA, *Sprechsaal* **122** (1989) 341.
2. N. KIMURA, S. ABE, J. MORISHITA and H. OKAMURA, in "*Sintering* ' 87", edited by S. Somiya, M. Shimada, M. Yoshimura and R. Watanabe (Elsevier Applied Science, London, 1988) p.1142.
3. S. LAWSON, PhD thesis, University of Sunderland, UK (1993).
4. M. YOSHIMURA, *Am. Ceram. Soc. Bull.* **67** (1988) 1950.
5. S. LAWSON and P.A. SMITH, *J. Am. Ceram. Soc.* **76** (1993) 3170.
6. K. TSUKUMA, Y. KUBOTA and T. TSUKIDATE, in "Advances in Ceramics", Vol.12, "Science and Technology of Zirconia II", edited by N. Claussen, M. Ruhle and A.H. Heuer (American Ceramic Society, Columbus, OH, 1984) p.382.
7. T. SATO and M. SHIMADA, *J. Am. Ceram. Soc.* **68** (1985) 356.
8. M. YOSHIMURA, T. NOMA, K. KAWABATA and S. SOMIYA, *J. Mater. Sci. Lett.* **6** (1987) 465.
9. F. F. LANGE, G. P. DUNLOP and B. I. DAVIES, *J. Am. Ceram. Soc.* **69** (1986) 237.
10. S. SCHMAUDER and H.SCHUBERT, *ibid.* **69** (1986) 534.
11. G.P. DRANSFIELD, K. A. FOTHERGILL and T. A. EGERTON, in "*Euro-Ceramics*", Vol. 1, edited by G. de With, R.A. Terpstra and R. Metselaar (Elsevier Applied Science, London, 1989) p.275.
12. A.D. SAVILL, PhD thesis, Nottingham University (1974).
13. S. LAWSON, G. P. DRANSFIELD, P. McCOLGAN, A. G. JONES and M. W. RAINFORTH, Presented at the 8th CIMTEC-World Ceramic Congress, Florence, Italy, June–July 1994.
14. C.-M. HWANG and I.-W. CHEN, *J. Am. Ceram. Soc.* **73** (1990) 1626.

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