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Tetragonal Zirconia Polycrystal (TZP)—A Review

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SUMMARY

Tetragonal zirconia polycrystal (TZP) is a new type of zirconia-based engineering ceramic. TZP ceramics are attractive because of their excellent room-temperature mechanical properties, which include flexural strength values over 1 GPa and a fracture toughness greater than 15 MPa m$^{1/2}$*. These, combined with superior wear properties and a thermal expansion coefficient close to that of iron and iron-based alloys, give rise to a class of desirable engineering ceramics.*

This review will attempt to summarise the considerable amount of work done on the microstructural development and mechanical properties of TZP, especially over the last few years. The paper is divided into four main sections:

- *(a) The* ZrO_2*–*Y_2O_3 *phase diagram.*
- *(b) Development and optimisation of Y-TZP.*
- *(c) Low-temperature ageing of TZP.*
- *(d) TZP developed by means of the* ZrO_2*–*CeO_2 *system.*

1 INTRODUCTION

Considerable interest is being shown in tetragonal zirconia polycrystalline (TZP) ceramics. These materials possess highly desirable mechanical properties at room temperature, including strength values over 1 GPa and a fracture toughness greater than 15 MPa m$^{1/2}$. They also exhibit excellent wear properties and have a thermal expansion coefficient close to that of iron and iron-based alloys. Such properties can be considered of great advantage in engineering applications.

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Metastable TZP materials are usually fabricated in the ZrO_2-Y_2O_3 system as a consequence of the wide range of yttria solubility in tetragonal zirconia and the low eutectoid temperature. This system is also believed to have a comparatively large critical particle size, below which retention of the tetragonal phase will be achieved at room temperature. These factors combine to make TZP production comparatively easy in this system. Recently interest has also been shown in the potentially more economic ZrO_2–CeO_2 system.

The high strength and toughness of TZP is considered to be largely due to the stress-induced martensitic transformation of the metastable tetragonal phase to the stable monoclinic phase. Unfortunately, the advantages afforded by this transformation have to be balanced against the disadvantages, particularly with regard to the effects of low-temperature ageing and the depreciation in properties as the temperature approaches the transformation temperature.

The common notation used in TZP literature involves placing the cation symbol of the stabilising oxide before the TZP abbreviation. In some cases the molarity of the stabilising oxide will be indicated by a number before the cation symbol, e.g.

$$ZrO_2\text{–}3\,\text{mol\%}\ Y_2O_3 = 3\text{Y–TZP}$$

Symbols corresponding to non-stabilising additions will be placed behind the abbreviation. These additions will be given as weight percentages, e.g.

$$ZrO_2\text{–}3\,\text{mol\%}\ Y_2O_3\ \text{plus}\ 20\,\text{wt\%}\ Al_2O_3 = (3\text{Y–TZP})20\text{A}$$

This notation will be adhered to throughout the account.

In this review an attempt will be made to assemble the existing work on TZP. It will then be possible to appreciate the potential of TZP as an engineering ceramic.

The work is divided into four parts as follows:

(a) The ZrO_2–Y_2O_3 phase diagram.
(b) Development and optimisation of Y–TZP.
(c) Ageing of TZP materials.
(d) Ce–TZP.

2 THE ZrO_2–Y_2O_3 PHASE DIAGRAM

The phase relationships in the ZrO_2–Y_2O_3 system have been extensively studied.[1–7] The general form of the diagram at low yttria contents is not in doubt and Fig. 1 follows from the work of Scott.[4]

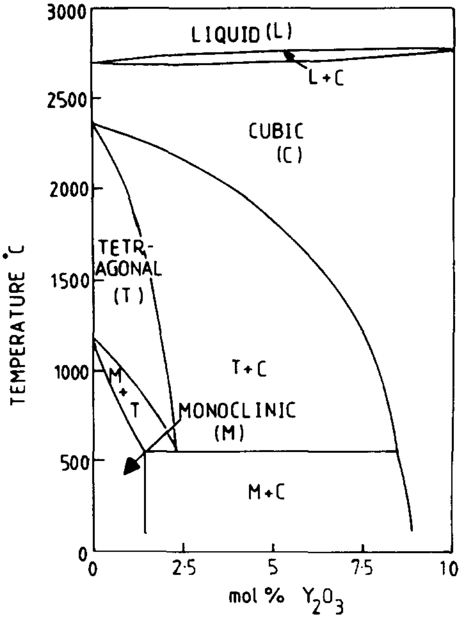


Fig. 1. Phase diagram for the zirconia-rich portion of the zirconia–yttria system.[4]

The exact position of the tetragonal to tetragonal and cubic phase boundary in the range 1300 to 1600°C is still open to question since there are a number of contradictions in the literature. Since this temperature range encompasses the conditions in which Y–TZP is sintered, the continuing debate is of considerable interest to those working on TZP. The reasons for the uncertainties are concerned with the proper attainment

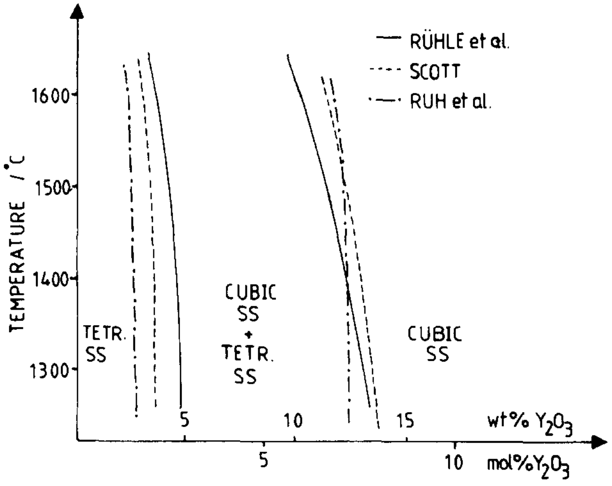


Fig. 2. Comparison of part of the ZrO_2–Y_2O_3 phase diagram for different studies.[4,7,8]

of the equilibrium phase distribution, even at these high temperatures. Because of the varying spatial distributions of yttria in commercial Y–TZP powders,[8] it is difficult to determine if equilibrium is ever established in Y–TZP production. The variation in the position of the phase boundary for three studies is shown in Fig. 2.

This uncertainty makes for considerable difficulties in the prediction of the extent of cubic formation during the sintering of Y–TZP. However, homogeneous powders containing more than 2Y generally yield significant amounts of cubic (>10%) when sintered above 1500°C. For example, Lange *et al.*[9] found cubic in 2·3Y–TZP heat-treated above 1450°C. It can therefore be concluded that by no means all TZP materials consist entirely of a metastable tetragonal phase.

Comparison of the ZrO_2–Y_2O_3 phase diagram with that of the ZrO_2–MgO system (Fig. 3) or the ZrO_2–CaO system highlights some of the advantages of the ZrO_2–Y_2O_3 system in TZP production. Commercial PSZ materials[10] are usually produced in the ZrO_2–MgO system[11] and this can be suitably compared.

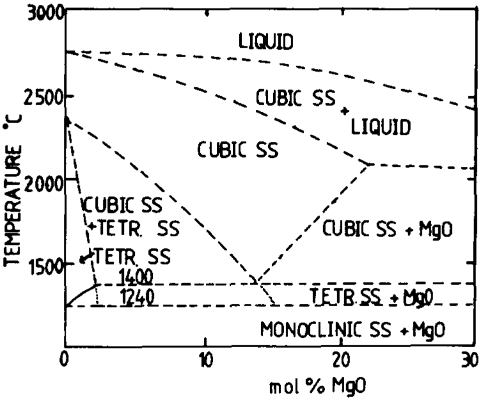


Fig. 3. Phase relations in a portion of the system ZrO_2–MgO.[11]

The first of these advantages is the larger range of solid solubility for yttria in tetragonal zirconia; this can be up to 2 or 3 mol% Y_2O_3 in the sintering temperature range of TZP. In contrast, the maximum solubility of magnesia in tetragonal zirconia is less than 1 mol% MgO. Hence the compositional range which offers the potential for metastable tetragonal materials is more extensive in the ZrO_2–Y_2O_3 system. This enables a certain degree of flexibility in fabrication condition. Thus the manufacturer has a choice of variables when adapting Y–TZP to suit the requirements of a specific application. For example, imparting superior ageing resistance to a TZP can be achieved by increasing the yttria content rather than trying to reduce the grain size and improving densification. The ageing behaviour of Y–TZP will be considered later in some detail.

The second major advantage concerns the decomposition of both tetragonal and cubic solid solutions during cooling from the sintering temperature. This is not a problem for Y–TZP because the eutectoid temperature is approximately 550°C.[4] As a consequence diffusional decomposition of the forementioned solid solutions is far too slow to be of significance. In contrast, the eutectoid temperature in the ZrO_2–MgO system is 1400°C. Hence control of the diffusional decomposition during fabrication and its use are of prime importance to the mechanical properties of Mg–PSZ.[12]

The available ZrO_2–CeO_2 phase relations show similar advantages.[13] Hence the potential for useful Ce–TZP is also being exploited and a Japanese commercial product has recently become available.

3 THE DEVELOPMENT AND OPTIMISATION OF Y–TZP

Gupta *et al.*[14–16] and Rieth *et al.*[17] were among the first to report the fabrication of TZP. Gupta's materials were dense and fine-grained. He did not specify the stabiliser content, preferring to disclose only that the structures were achieved with small quantities of yttria and other rare earth additions.

The greater part of Gupta's work concerned the effect of sintering temperature and time on the stability of the tetragonal phase. This was studied indirectly by its effects on density and mechanical properties. Lange[18] and Matsui *et al.*[19] have also studied such relationships for Y–TZP. Figure 4 shows the relationship between the sintering temperature and the sintered density for samples fired by Gupta[14] for 2, 5 and 15 h.

The plots show a maximum for the sintered density between 1400 and 1500°C. The increase in density at temperatures lower than this range is thought to be due to densification.[14] Lange[18] also established an increase in tetragonal content with increasing sintering temperature which could contribute to the increase in density. Gupta did not observe any change in tetragonal content below the peak density and thus attributed the increase in density solely to increased densification. At temperatures above that at which the peak density is obtained, there is a gradual decrease in density. Gupta[14,15] observed a sudden decrease in the tetragonal content of the as-sintered surface and attributed the gradual decrease in density to the tetragonal (t) to monoclinic (m) martensitic transformation on cooling. The authors state that the grain size developed at those sintering

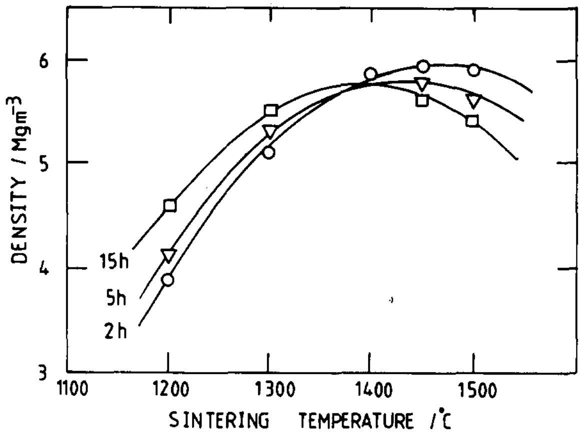


Fig. 4. Density–temperature relation in tetragonal zirconia.[14]

conditions exceeded the critical grain size for spontaneous t–m transformation on the sample surface. The cracking which accompanied the transformation on the surface reduced the overall density. Matsui *et al.*[19] observed a similar trend in strength results for 3Y–TZP at different sintering temperatures, the underlying cause being the same as for the variation in density.

Gupta[16] established a relationship between the amount of t–m transformation on a sample surface and the strength of the sample. This is shown in Fig. 5. This clearly indicates that when the amount of untransformed material decreases below 30% there is a drastic decrease in strength. The authors attributed this to the formation of surface cracks in the samples with greater than 70% surface transformation. The cracks are caused by the anisotropic expansion accompanying the t–m transformation on cooling from the sintering temperature.

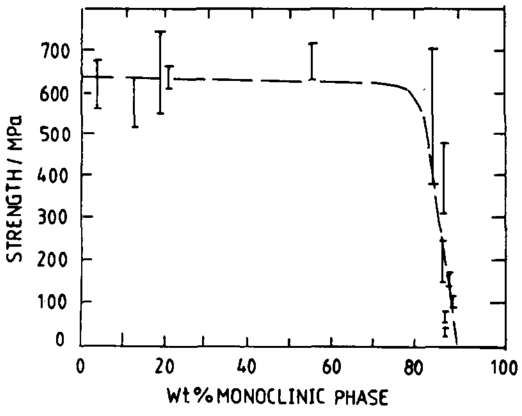


Fig. 5. Strength versus monoclinic content in TZP.[16]

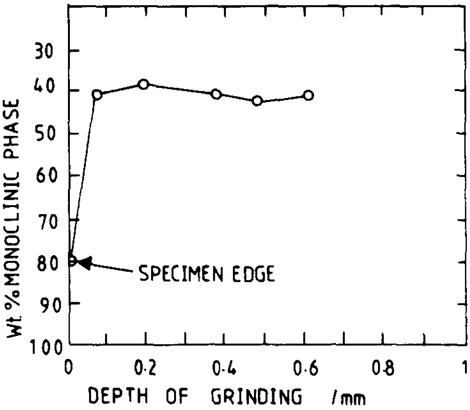


Fig. 6. Tetragonal content versus depth of grinding for TZP with high surface monoclinic content.[15]

Gupta *et al.*[15] also showed that the monoclinic content of the ceramic varied with depth below the sample surface. As shown in Fig. 6, a specimen which shows an 80% transformation on the surface when carefully polished shows only a 40% transformation below a surface layer less than 100 μm thick. It is not clear if this 40% transformation is respresentative of the bulk structure or if it resulted from the polishing treatment.

Gupta *et al.* achieved strengths between 600 and 700 MPa for peak density materials. X-ray analysis of fracture surfaces revealed that about 40% transformation had occurred on fracture by stress-induced transformation. The high strength of these samples was attributed to this mechanism. The fracture toughnesses of the materials were in the range 6 to 9 MPa $m^{1/2}$ measured by the indentation technique.

The authors[15] also attributed the effect of sintering temperature on strength as being due to the change in the grain size. Figure 7 illustrates clearly the existence of a critical grain size above which there is a rapid decrease in strength. This grain size was reported to be approximately 0·3 μm.

The rapid increase in strength with decrease in the grain size in the range 0·34 to 0·3 μm cannot be explained by a conventional decrease in flaw size with grain size argument. It can be explained as an increasing contribution of the stress-induced phase transformation. The low strength samples with grain sizes above 0·34 μm showed cracking on external surface accompanying large amounts of t–m transformation. This supports the existence of a critical particle size for TZP and is consistent with the concept of the constrained transformation.[20]

Constrained transformation theory also indicates that such a transformation can be effected by stabiliser content. Various authors[18,19,21,22] have

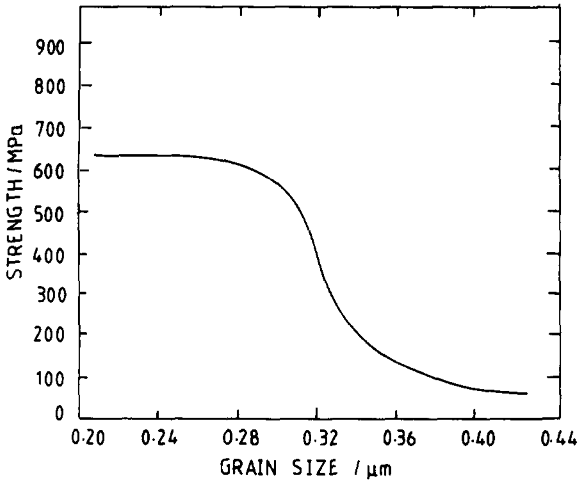


Fig. 7. Strength versus grain size for TZP.[16]

studied this effect on both physical and mechanical properties. Lange[18] compared grain size measurements with phase contents of as-sintered surfaces. Figure 8 shows how the stabiliser content was found to affect the critical grain size on an as-sintered surface.

High tetragonal contents could not be achieved below 2Y and the critical grain size rises sharply between 2Y and 3Y. Unfortunately the sintered densities of Lange's specimens were in the range 80–90% of theoretical, and larger critical grain sizes might well have been achieved with a dense

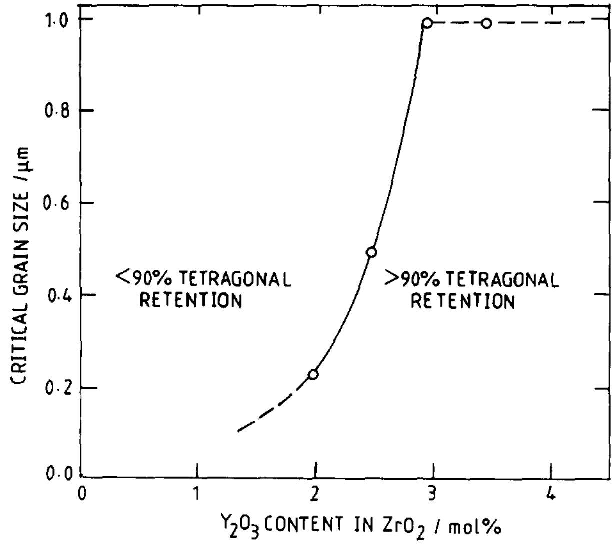


Fig. 8. Critical grain size plotted against Y_2O_3 content in tetragonal zirconia.[18]

ceramic. Haberko and Pampuch[21] also observed a large increase in critical grain size between 2Y and 3Y.

The effect of stabiliser content on mechanical properties has been well studied.[18,21,22] A comparison of the toughness results is given in Fig. 9.

As can be seen the trends in the results of all three studies are in fair agreement. The maximum toughness in each study occurred at about 2Y. All the authors agree that the decrease in toughness below 2Y is due to spontaneous transformation of the tetragonal phase to the monoclinic phase subsequent to cooling from the sintering temperature. The monoclinic formation results in microcracking of the ceramic and also in a decrease in fracture toughness. Tsukuma *et al.*[22] achieved the highest maximum toughness of 10 MPa m$^{1/2}$. The gradual decrease in toughness between 2Y and 6Y was attributed by Lange[18] to a decrease in the volume fraction of transformable tetragonal phase due to the development of non-transformable cubic phase. Tsukuma *et al.*[22] have agreed with this explanation and clearly identified large cubic grains containing 6·9Y. The smaller grains of monoclinic phase contained 1·8Y and are thought to have been tetragonal prior to the stress-induced transformation. In contrast, Haberko and Pampuch[21] did not identify cubic phase in TZP containing less than 5Y. This was probably due to the very low sintering temperatures employed and good chemical homogeneity of the powders which helped to avoid cubic phase formation. So in the absence of cubic phase Haberko attributed the slow decrease in toughness, at compositions above 2Y, to a general effect, that of the decrease in chemical-free energy on the fracture

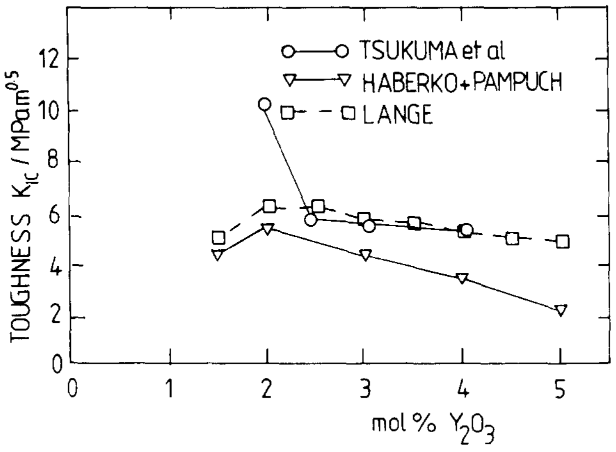


Fig. 9. Dependence of fracture toughness on Y_2O_3 content from three different studies.[18,21,22]

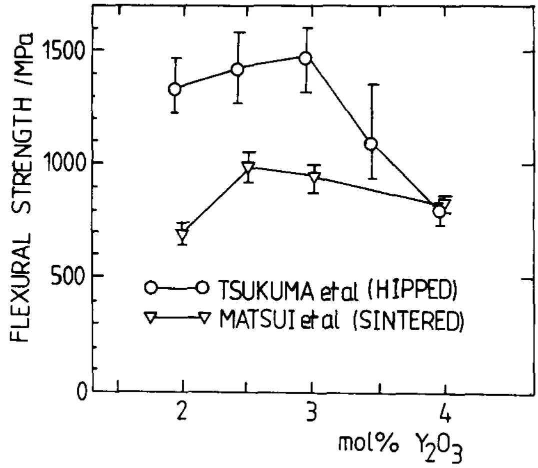


Fig. 10. Dependence of bend strength on Y_2O_3 content for hot-pressed[22] and sintered[19] materials.

energy. Because of the known difficulty in quantitative determination of cubic phase by X-ray diffraction analysis,[23] it may well be that the authors were unable to distinguish the cubic and tetragonal phases.

It was expected that the effect of yttria content on strength would reflect the variation in toughness. The variation in strength of hot-pressed[22] and sintered[19] TZP with yttria content is shown in Fig. 10.

It is apparent that the strength results show the same trends as toughness but the peak strength is displaced from 2·5Y to 3Y in comparison with the peak toughness at 2Y.

The decrease in strength below 2·5Y is due to the spontaneous t–m transformation on cooling from the sintering temperature which increases the critical flaw size and thus reduces strength. Above 3Y the strength decrease is thought to be due to the decrease in toughness corresponding to the development of non-transformable cubic phase. Lange[18] observed that materials with less than 2Y, which contained larger amounts of monoclinic, showed clear intergranular fracture as shown in Fig. 11(a). This suggests the formation of extended intergranular microcracks on cooling. The microcracks are responsible for the low strength of these materials. Tetragonal materials showed irregular transgranular fracture (Fig. 11(b)). Lange attributed this to crack interactions with monoclinic twins in grains which transformed ahead of the crack. The cubic grains in materials of higher yttria content showed smooth transgranular fracture (Fig. 11(c)).

As expected, Tsukuma's hot isostatically pressed (hipped) material[22] showed higher strength than Matsui's sintered material,[19] because of the

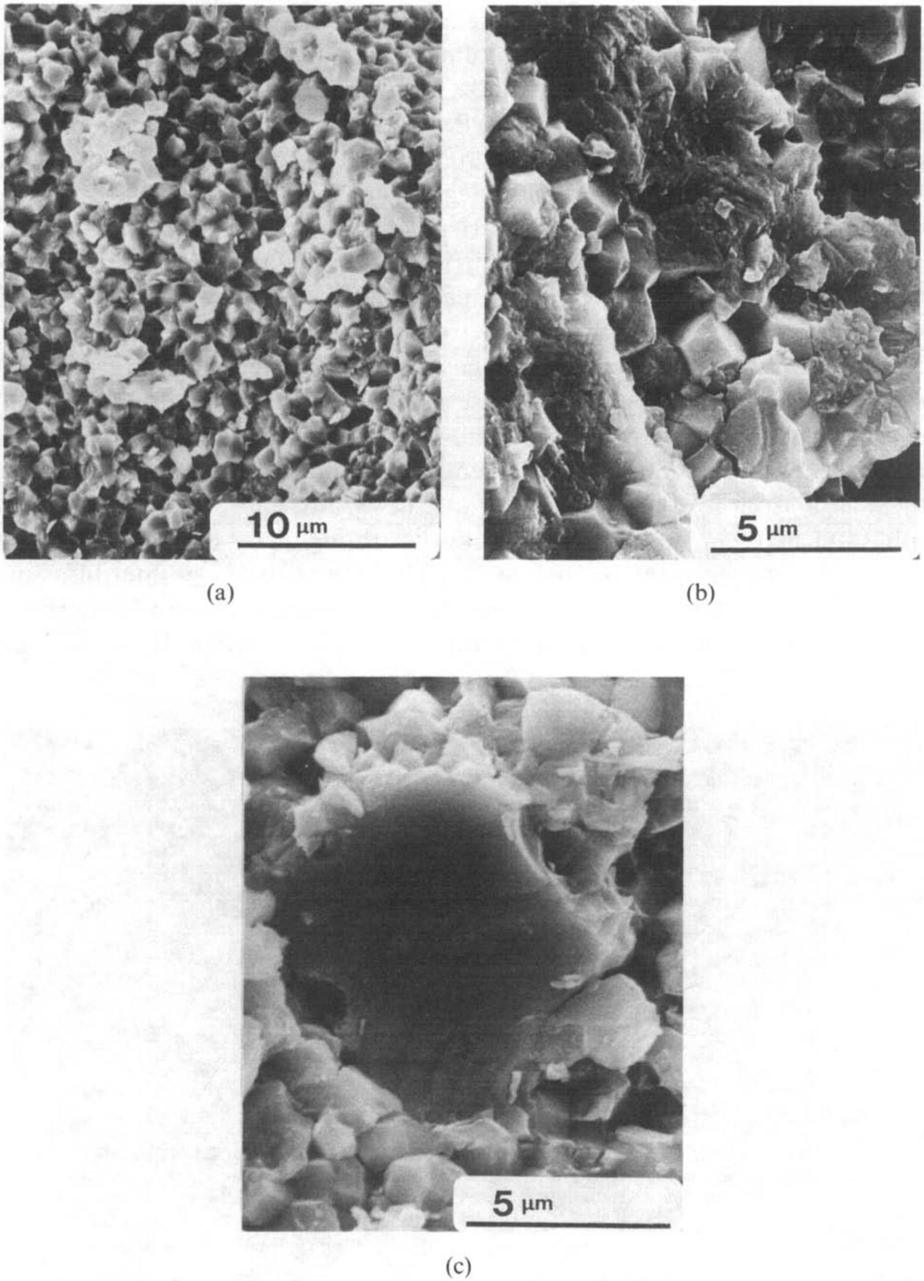
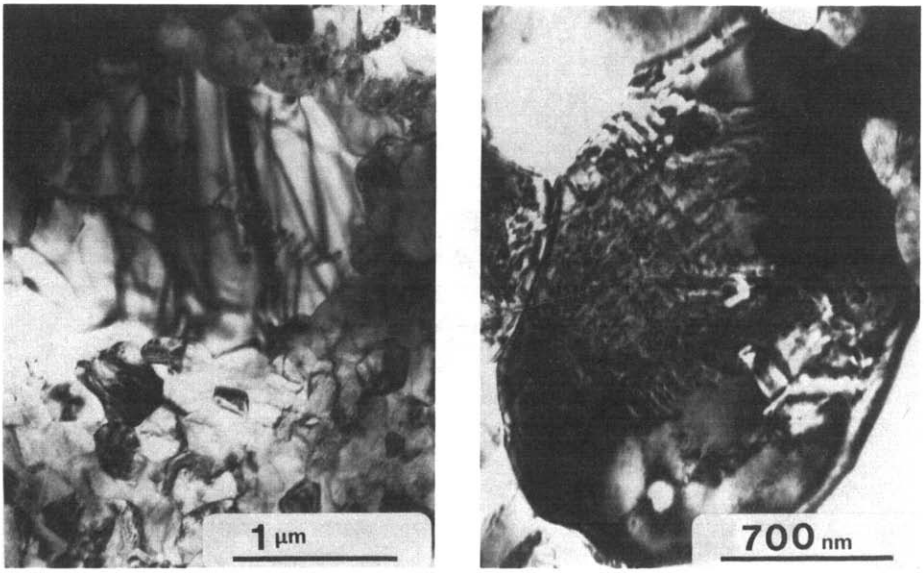


Fig. 11. Fractography of TZP.[24] (a) Smooth intergranular fracture of monoclonal phase. (b) Irregular transgranular fracture of tetragonal phase. (c) Smooth transgranular fracture of cubic phase.

reduction of critical flaw size by hipping. Hipping produced almost theoretical density but the final density was dependent upon the pre-hipping sintering treatment. Tsukuma *et al.*[22] found that the lowest pre-sintering temperature used, 1400°C, produced the best hipped strength irrespective of hipping operation. Pre-sintering at higher temperatures produced porosity which was not eliminated during hipping. The reasons for the increased porosity are not clear.

A microstructural study of a variety of commercial Y–TZP has been completed by Rühle *et al.*[8] The yttria content of the materials studied ranged from 3·5 to 8·7 wt%. Most specimens were two phase mixtures of tetragonal and cubic phases similar to the microstructure in Fig. 12(a).

The grain size of the tetragonal phase varied between 0·2 and 2 μm. The spatial distribution of yttria in these grains varied considerably, even in specimens fabricated from chemically homogeneous powders. In such a material the yttria content in the centre of a grain (3·2 ± 0·2 wt% Y_2O_3) increased to 3·7 ± 0·2 wt% Y_2O_3 at the grain edge. More extensive inhomogeneity was discovered in ceramics thought to be fabricated from chemically inhomogeneous powders. This reflects the slow interdiffusion in the ZrO_2–Y_2O_3 system at the lower sintering temperatures and underlines the importance of chemical homogeneity of the powder. It is also the



(a) (b)

Fig. 12. (a) Large cubic grain surrounded by smaller tetragonal grains.[25] (b) Tetragonal precipitates in a cubic grain.[25]

apparent reason why strength did not correlate well with grain size in this study. The authors state that yttria content and spatial distribution had considerable effect on the transformability of thin sections of tetragonal grains during transmission electron microscopy (TEM) *in situ* straining experiments. Hence it would be expected that chemically inhomogeneous powders of similar overall composition and grain size would produce a more transformable TZP than a homogeneous powder. The inhomogeneous material would contain tetragonal grains of low yttria content, in which the transformation could nucleate. The authors[8] witnessed the nucleation of the transformation in regions of high stress near the grain boundaries and at intergranular defects. The transformational strain frequently nucleated the reaction of adjacent grains. Interestingly, the authors[8] observed slow progression of the transformation through tetragonal grains with higher yttria contents. If this is not due to the presence of defects, it must be concluded that the martensitic transformation is not entirely nucleation controlled in such grains.

The larger cubic grains also showed considerable variation in yttria content, ranging from 9·3 to 12 wt% Y_2O_3. Usually the cooling rate from the sintering temperature is slow enough to allow diffusional controlled, homogeneous nucleation of tetragonal precipitates in the cubic grains (Fig. 12(b)).[25] If very fast cooling rates are employed a diffusionless shear transformation of the cubic to t′ may be observed.[4,23,26,27] t′ is thought to be a tetragonal phase of higher yttria content than the equilibrium tetragonal phase. The t′ phase does not undergo the stress-induced transformation[26] and has been observed by TEM[27] and X-ray diffraction.[23]

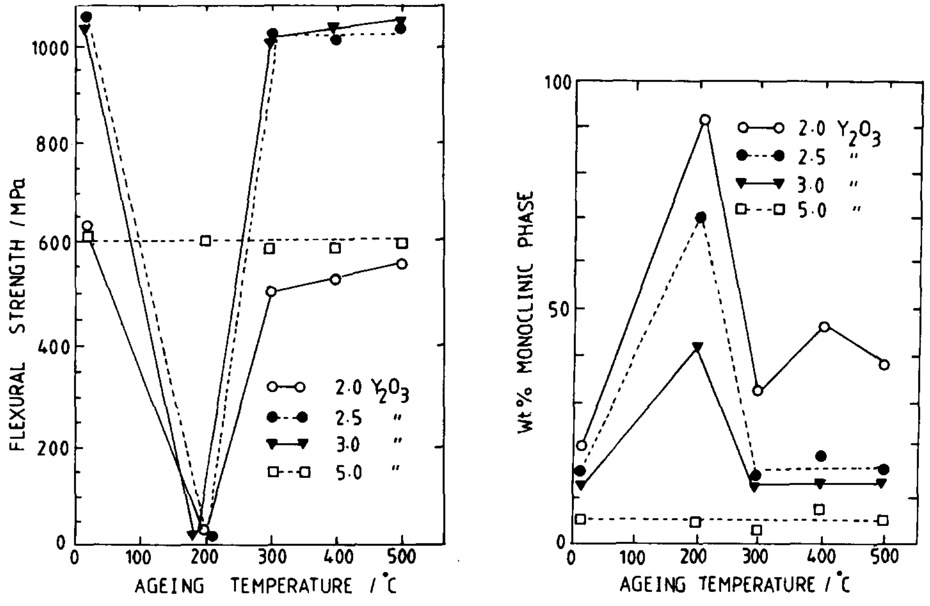
A common microstructural feature in TZP is a continuous grain boundary phase between 2 and 10 nm thick. This phase has been shown to contain yttria, silica, alumina and possibly zirconia and is thought to be a low-viscosity liquid phase in the Al_2O_3–Y_2O_3–SiO_2 system which exists between 1300 and 1400°C.[8] It is generally considered that this aids liquid phase sintering in TZP; some rounded grains and triple point pockets observed by TEM support this theory.[8] However, the nature of this grain boundary phase and its effects on densification are yet to be clearly understood.

4 AGEING OF TZP MATERIALS

The effects of ageing at low temperature on yttria-stabilised zirconia were first communicated by Kobayashi *et al.*[28] Sato and Shimada[29] reported the effects of ageing for 50 h in air in the temperature range 100 to 500°C for 3Y–TZP. For specimens sintered between 1400 and 1600°C a maximum amount of monoclinic was found on the sample surface in the ageing temperature range 200 to 250°C. It was also shown that cracking was associated with the surface transformation. The cracks progressed into the specimen interior in conjunction with the transformation.

As would be expected such ageing behaviour seriously affected the mechanical properties of the TZP material. The phenomena of ageing and their influence on strength for different TZP materials are well known.[19,22,30,31] A comprehensive study of the variation in strength with ageing temperature was carried out by Masaki.[31] In this work chemically homogeneous powders of 2Y, 2·5Y, 3Y, 4Y and 5Y were sintered, hot pressed and hipped. Specimens were then aged for various times from 100 to 8000 h in air in the temperature range 150 to 500°C. The relationship between strength and ageing temperature for samples sintered at 1500°C for 2–3 h and then aged for 2000 h is shown in Fig. 13(a). The sintered densities of the specimens were always greater than 97% of theoretical density. Figure 13(b) shows the relationship between surface monoclinic content and ageing temperature for the same samples.

It can be seen that the change in surface monoclinic content correlates well with the change in strength. The results are consistent with the



(a) (b)

Fig. 13. (a) Bend strength versus ageing temperature for Y–TZP.[31] (b) Surface monoclinic content versus ageing temperature for Y–TZP.[31]

hypothesis that surface cracking due to the tetragonal to monoclinic phase transformation is responsible for the decrease in strength between 200 and 300°C.

The underlying mechanism responsible for the transformation during ageing is not clear. However, various explanations based on chemical corrosion at the grain boundaries will be discussed. A body of opinion[32] considers that some unknown chemical processes are relieving the matrix constraint on surface grains by attacking the grain boundaries. This would then allow the surface grains to transform. The reason why no degradation is seen above 300°C is thought to be insufficient undercooling to drive the martensitic reaction. It is interesting to compare the low-temperature ageing behaviour of MgO partially stabilised zirconia (Mg–PSZ) which does not have as much transformable material adjacent to the grain boundaries. As expected Mg–PSZ does not exhibit the strength degradation of Y–TZP on low-temperature ageing.

It is expected that there is a critical grain size for the surface transformation observed in Y–TZP during low-temperature ageing and that this behaviour can be altered by varying the yttria content and the grain size. Matsui *et al.*[19] sintered 3Y–TZP at 1400°C for 3 h and 1300°C for 2 h. The grain sizes were 0·5 and 0·2 μm, respectively. The latter showed no surface transformation on ageing, demonstrating strong support for the expectation of a critical grain size for the surface transformation during ageing.

Masaki[31] aged hot-pressed (HP) and hipped materials for 2000 h over the temperature range 150 to 500°C. 2Y–TZP was the only material sensitive to ageing. The grain sizes of the HP and hipped materials were similar to that of sintered material and so the increased resistance to the transformation on ageing was attributed to the very high density ($>$99·5%) achieved with the HP and hipping methods. The sintered material densities were only greater than 97% of theoretical density.

Watanabe *et al.*[30] sintered 2Y–TZP up to 5Y–TZP in the temperature range 1400 to 1600°C. They found that materials containing less than 4Y suffered a dramatic loss of strength after only 100 h ageing in the temperature range 200 to 300°C. Their results for critical grain size for the surface transformation against yttria content are shown in Fig. 14.

A possible reason why the results do not agree with other work[22,32] may be the different powder preparation route. Watanabe *et al.*[30] used a mixed oxide powder preparation route which is likely to cause more chemical inhomogeneity in the sintered product than the coprecipitation routes used in the other studies. Chemically homogeneous powders give the most uniform spatial distribution of Y_2O_3 in the sintered product and this may account for the improved resistance to ageing of the materials

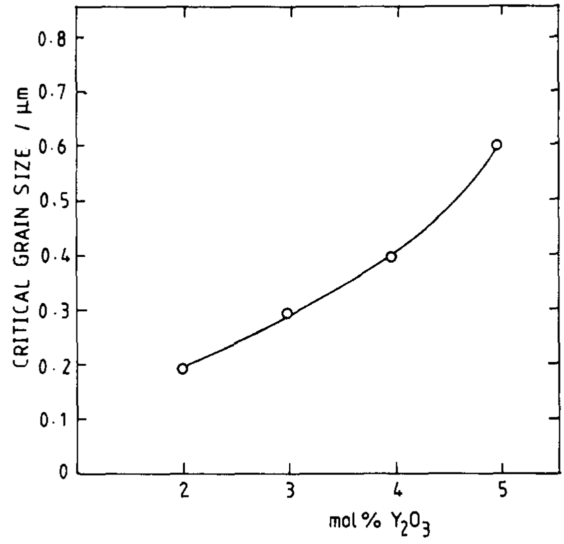


Fig. 14. Critical particle size versus yttria content for samples held at 300°C for 1000 h.[30]

produced by Tsukuma[22] and Masaki.[31] Here again the importance of the chemical homogeneity of the starting powders in relation to the mechanical properties is made apparent.

The development of strength degradation with ageing time at 230°C was studied by Tsukuma *et al.*,[22] for 3Y–TZP. Materials with grain sizes greater than 1 µm showed 50% transformation on the surface after ageing for 1200 h and this coincided with a smooth decrease in strength from 900 to 100 MPa over the period 0 to 1200 h. Materials with grain sizes smaller than 0·4 µm showed no decrease in strength over the same ageing time range. Tsukuma[22] also studied the effect of ageing time on strength for different compositions. The ageing temperature used was 300°C and all the materials had a tetragonal grain size of 0·4 µm. They found a critical yttria content below which there was extensive surface transformation after ageing times as low as 24 h. This critical yttria content was 1·9Y; these samples showed a decrease in strength from 1100 MPa to less than 500 MPa on ageing.

It is to be expected that Y–TZP would also suffer strength degradation during thermal cycling. Matsui *et al.*[19] studied the thermal expansion hysteresis of 3Y–TZP sintered at 1300, 1400 and 1500°C for 3 h. The sintering schedules gave grain sizes of 0·2, 0·5 and 1·5 µm, respectively. The grain size dependence of the thermal expansion hysteresis is shown in Fig. 15.

On cooling the 3Y–TZP sintered at 1500°C shows a sudden volume increase corresponding to the volume change accompanying the tetragonal

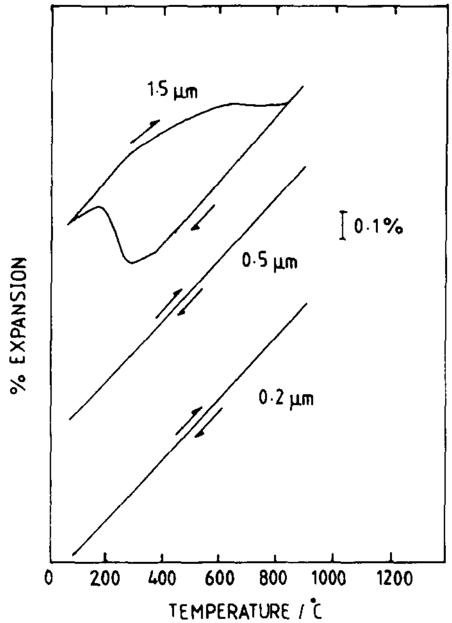


Fig. 15. Thermal expansion curves for 3Y–TZP materials with three different grain sizes.[19]

to monoclinic transformation. The reverse transformation on heating occurs at around 800°C. Such thermal expansion behaviour would seriously degrade the mechanical strength. The finer grain size materials did not exhibit thermal expansion hysteresis because the tetragonal phase is retained after the thermal cycling.

Watanabe *et al.*[30] measured the thermal expansion hysteresis dependence on yttria content, for materials sintered at 1500°C for 1 h. They showed that 2Y–TZP and 2·5Y–TZP exhibited thermal expansion hysteresis for the same reasons as described above. The 2Y–TZP showed the greater thermal expansion hysteresis because more material underwent the martensitic transformation during thermal cycling. 4Y–TZP showed no hysteresis. The authors' observations are consistent with the effect of yttria content on transformation behaviour.

Tsukuma *et al.*[22] carried out thermal cycling tests on materials of differing yttria content, having a uniform grain size of 0·4 μm. Only 1·9Y–TZP showed significant amounts of surface transformation and strength degradation when cycled three times between 800 and 20°C. Matsui *et al.*[19] also creep tested 3Y–TZP sintered at 1400°C for 3 h, under a load of 400 MPa. Creep deformation was observed only in the temperature range in which surface transformation occurred during low-temperature ageing. The maximum creep rate was at 250°C.

Little work has been undertaken to improve the resistance of existing

Y–TZP materials to strength degradation on low-temperature ageing. One approach taken by Schubert *et al.*[33] was to protect the surface with a layer of overstabilised material comprised of non-transformable cubic phase. This can be achieved by sintering the compact in a powder bed made up of the stabilising oxide. The surface layer of such samples then remains untransformed after autoclaving which caused significant transformation in the uncoated samples. Hence coating is a simple method of preventing surface transformation during low temperature annealing. Unfortunately, the large cubic grains on the surface may increase the critical flaw size and thus reduce the strength of the ceramic. Another approach taken by Matsumoto[34] is high temperature annealing of aged TZP, which has been shown to cause almost total strength recovery. Other attempts to prevent strength degradation have been concerned with the production of new materials by the addition of Al_2O_3 or alternative stabilising agents to existing Y–TZP materials. These materials will be discussed later.

First it is intended that the underlying reasons and available experimental evidence for the low-temperature ageing behaviour should be examined. Sato *et al.*[35] annealed 2Y–TZP, 3Y–TZP and 4Y–TZP at 200°C for 50 h. They observed the expected surface transformation accompanied by microcracking. More interestingly they observed that water and some non-aqueous solvents accelerated the tetragonal to monoclinic transformation and that specimens annealed under vacuum showed much lower rates of surface transformation.

Nakajima *et al.*[36] sintered materials in the composition range 2 to 5 mol% Y_2O_3 at 1550°C for 2 h and then dipped them in aqueous solutions of sulphuric acid, nitric acid and sodium hydroxide. The specimens were immersed for up to 150 h in the temperature range 41 to 107°C. Other specimens were autoclaved in distilled water at temperatures between 100 and 180°C.

Immersion at temperatures greater than 63°C caused an increase in the surface monoclinic content. As expected 2Y–TZP showed the most significant increase in monoclinic fraction, of approximately 20% at 107°C. Other compositions also developed slight increases in surface transformation. It was found that in tests below 107°C a saturation in the amount of transformation was achieved after about 60 h.

Autoclaving in water above 100°C also caused surface transformation, especially above 140°C, when all the transformable tetragonal on the surface became monoclinic only after a few hours. This caused severe cracking and even disintegration in the lower yttria content materials.

Sato and Shimada[32] cast further light on the reasons for strength degradation on low temperature annealing. They sintered 2Y to 6Y materials in the temperature range 1400 to 1600°C and then carried out

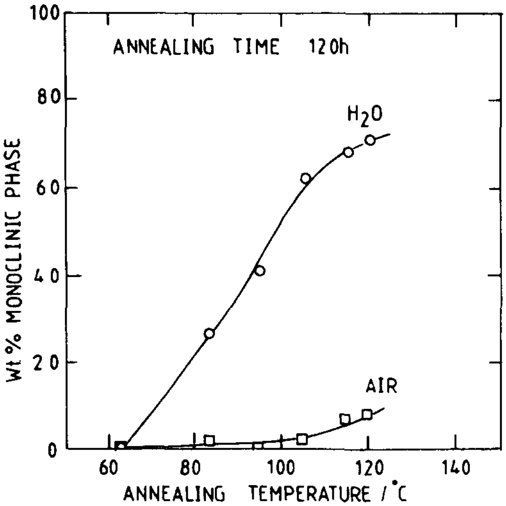


Fig. 16. Tetragonal to monoclinic phase transformation resulting from annealing in water and in air.[32]

low temperature annealing in water and other solvents. Figure 16 shows the difference in surface monoclinic content of 3Y–TZP after sintering at 1600°C and annealing in water and in air over the temperature range 60 to 120°C. Annealing in water greatly enhances the transformation. The authors also observed accelerated transformation on ageing at 95°C in certain non-aqueous solvents. Acid and base additions did not affect the transformation rate when ageing in water.

The mechanism by which water enhances the surface transformation is not clear but Sato and Shimada[32] ruled out dissolution of zirconia or yttria because no weight loss was detected after annealing.

Instead the increase in surface transformation is thought to be caused by a corrosion mechanism such as that attributed to vitreous silica by Michalske and Freiman.[37] The proposed reaction scheme between water and the Zr–O–Zr bond (Fig. 17) requires a solvent with a proton donor opposite a lone pair of electrons. The supporting evidence for this mechanism is indirect, in that aqueous and non-aqueous solvents with a molecular structure containing a lone pair opposite a proton donor site were found to accelerate monoclinic formation during ageing. The authors[32] believe that slow crack growth due to this mechanism is responsible for removing the mechanical constraint, thus destabilising the surface grains. The resulting transformation then produces even more cracking. Non-aqueous solvents containing a lone pair not directly opposite a proton donor site slightly accelerated the surface transformation, but this may have been due to traces of moisture in the solvents. Non-aqueous solvents containing no lone pair of electrons did not accelerate monoclinic formation.

Sato *et al.*[38] sintered 2Y–TZP, 3Y–TZP and 4Y–TZP at 1600°C for 3 h and then annealed specimens in the temperature range 100 to 600°C under controlled humidity conditions. The partial pressure of water was varied from 0·1 to 7350 Pa.

The proposed mechanism[32] does not require dissociation of water molecules or dissolution of reaction products so it was suspected that the reaction would also be accelerated by water vapour. Indeed, higher vapour pressures were found to give faster rates of transformation at temperatures lower than 200°C.[38] The maximum monoclinic formation was at 200°C, as observed for ageing in dry air, hence the equilibrium was not affected by the presence of water vapour. The monoclinic formation was also found to be first order with respect to the surface tetragonal content prior to ageing.

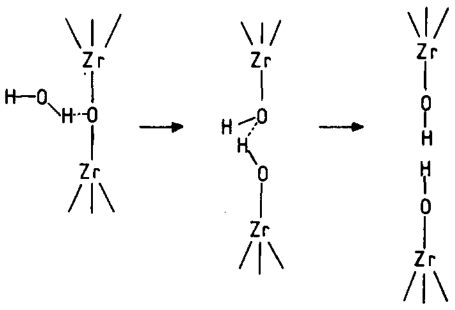


Fig. 17. The proposed reaction mechanism between water and the Zr–O–Zr bonds at the crack tip.[32]

Lange *et al.*[39] suggest that during the low-temperature ageing, water vapour reacts with yttria which was originally in solid solution in the zirconia. Observations of aged TEM foils revealed small clusters of crystallites (20–50 nm) on monoclinic as well as cubic grain boundaries. The crystallites were identified as α-yttrium hydroxide, and this was used as supporting evidence for their explanation of the phenomenon. Increasing the amount of grain boundary phase was found to have little effect on the ageing behaviour and so it was concluded that the grain boundary phase does not itself play a significant role in the ageing behaviour.

This alternative hypothesis thus involves the transformation of surface tetragonal grains to the monoclinic form when water vapour has drawn sufficient yttrium from the ceramic material adjacent to the grain boundary to form a monoclinic nucleus larger than the critical size. The entire grain will then undergo spontaneous martensitic reaction to monoclinic and the resulting microcracks will then expose further tetragonal grains to the environment.

Attempts have been made to improve the thermal stability of Y–TZP by the addition of various other oxides.[40,41] These additions can be split into two groups depending on whether the oxide forms a solid solution with zirconia or not.

Alloying Y–TZP with ceria caused grain growth, especially when sintered above 1500°C.[40,41] Increasing additions of ceria from 0 to 20 wt% caused a decrease in monoclinic formation on ageing in hot water.[40] In this study, it was found that 10 wt% CeO_2 addition to 3Y–TZP and 4Y–TZP and 15 wt% CeO_2 addition to 2Y–TZP completely inhibited the transformation on ageing. Addition of TiO_2 also increased the grain growth in Y–TZP and enhanced the stability of the tetragonal phase. However, only ceria additions below 6 mol% CeO_2 did not degrade the mechanical properties.[41]

Other known stabilising agents were also added to Y–TZP.[41] Additions of magnesia and calcia reduced the amount of transformation on ageing, but this was due to the increased volume fraction of cubic phase. In both cases the additive resulted in deterioration of the mechanical properties of the Y–TZP.

The retardation of surface transformation in Y–TZP, by the addition of alumina,[40] is due to the inhibition of grain growth of the tetragonal zirconia by the alumina grains. Its effect is to retard the transformation rate during ageing in water below 100°C.[40] However, the surface transformation is not completely inhibited.

Y–TZP–Al_2O_3 composites containing 0 to 40 wt% Al_2O_3 have also produced materials of very high strength. Tsukuma *et al.*[42,43] were the first to report the properties of this type of material. In their studies, the effect of alumina content on the strength and toughness in the temperature range 20 to 1000°C was measured.

Sintered specimens were prepared from sub-micron homogeneous composite powders and sintered at 1500°C for 1 h.[42] The strength and toughness of these sintered materials were the same or lower than the usual Y–TZP materials. When the materials were hipped there was a dramatic increase in strength associated with a relative density increase from 97 to 99%. The relationship between strength and alumina content for 2Y–TZP and 3Y–TZP is shown in Fig. 18.

The behaviour was independent of the yttria content, the maximum in the strength increment occurring at about 20 wt% Al_2O_3, which gave a fracture stress of 2·5 GPa. The indentation toughness and monoclinic content of the fracture surface do not correlate with the strength and hence transformation toughening is not thought to be responsible for the strength increase observed when the alumina content is increased.

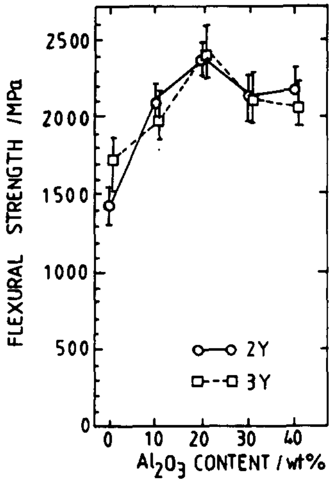


Fig. 18. Dependence of bend strength on alumina content for 2Y–TZP and 3Y–TZP.[42]

Figure 19 shows the decrease in toughness with increasing alumina addition for 2Y–TZP. The graph also shows the decrease in monoclinic content of the fracture surfaces. A more likely explanation for the increase in strength is a progressive decrease in the flaw size responsible for fracture. This would arise because of grain growth inhibition of the zirconia by the dispersed alumina phase during hot pressing. Thus the alumina addition may be affecting the critical flaw size rather than the fracture energy. The reason for a maximum in strength at 20 wt% Al_2O_3 is less clear; there may be a connection with the decrease in relative density above 20 wt% Al_2O_3.

Tsukuma *et al.*[43] also measured the variation in strength of hipped

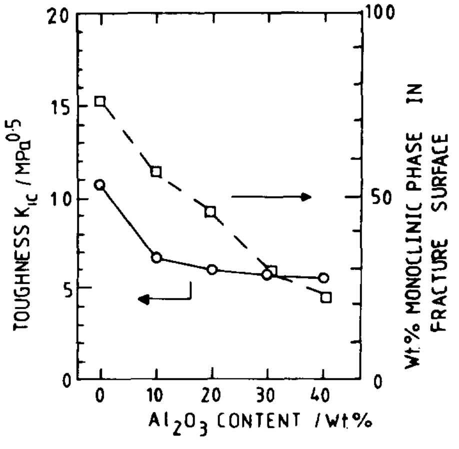


Fig. 19. Fracture toughness and monoclinic phase fraction on fracture versus alumina content of 2Y–TZP.[42]

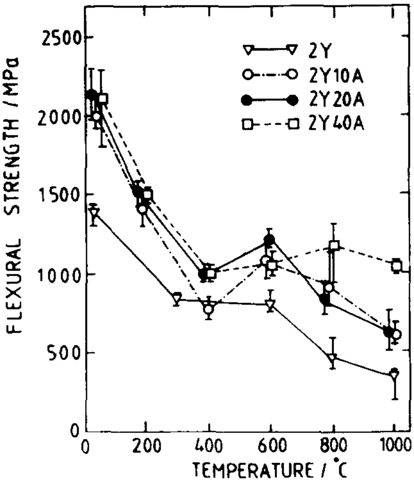


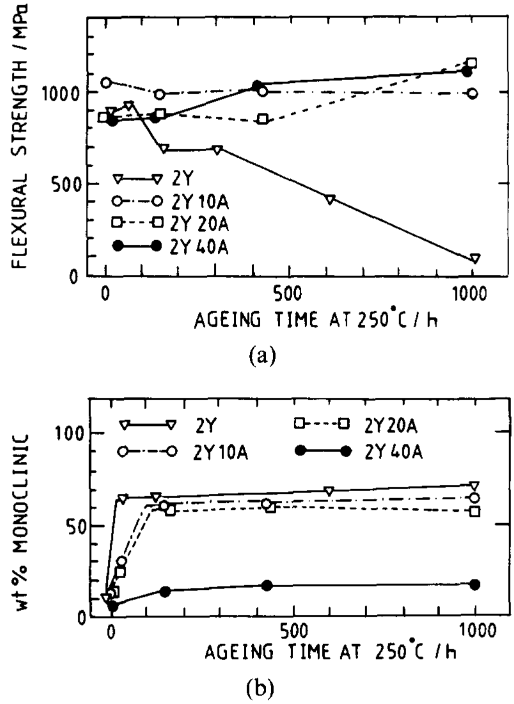
Fig. 20. Temperature dependence of bend strength for hipped 2Y-TZP-Al_2O_3 composites.[43]

composites between 20 and 1000°C. Figure 20 shows the temperature dependence of strength for 2Y–TZP with different alumina contents.

In comparison with Y–TZP, such composite materials have high room-temperature strength and also maintain an enhanced strength at high temperature. Unfortunately the fracture toughness of these materials was determined by a method sensitive to crack initiation and therefore showed the same trends as the strength results. For this reason we are unable to speculate about the extent of transformation and its effects on toughness. However, the composites do show the same trend of strength with test temperature as the Y–TZP material. One would expect the contribution of transformation toughening to decrease with increasing temperature and this may account for the decrease in strength of all the materials. The enhanced strength of the composites over the temperature range considered is again probably due to smaller critical flaws. However, the trend of strength with temperature for both Y–TZP and the composites is probably due to the effect of the reduced transforming volume on toughness and its consequent influence on strength.

Tsukuma and Shimada[44] also studied the effect of low-temperature ageing in air on the mechanical properties of the composite materials. From Fig. 21 it is apparent that increasing the alumina addition decreased the amount of surface monoclinic formed during ageing. The authors attributed this to the increased constraint given by the increasing addition of the high modulus second phase. All the materials were sintered between 1600 and 1400°C for 2 h and aged at 250°C for up to 1000 h.

The strength of 2Y–TZP decreased steadily with ageing time but all the



(a)

(b)

Fig. 21. (a) Bend strength versus ageing time for 2Y–TZP and 2Y–TZP–Al_2O_3 composites.[44] (b) Surface monoclinic content versus ageing time for 2Y–TZP and 2Y–TZP–Al_2O_3 composites.[44]

materials containing alumina showed no significant decrease in strength. At first sight it is quite surprising that composites containing less than 20 wt% Al_2O_3 do not show decreased strength, because they contain approximately 50 wt% of monoclinic phase in the transformed layer. Obviously the surface transformation in the composite materials has not significantly affected the critical flaw size.

The resistance to ageing of the composite materials may help provide the answer to the susceptibility of Y–TZP to low-temperature ageing and improve the suitability of these materials for automotive applications where their superior strength will be a distinct advantage. Although answers have apparently been found for the ageing problem, a firm understanding of the underlying mechanism remains elusive. It is important to understand the behaviour of TZP in such environments if they are to be used in engineering applications with confidence in their reliability. As far as ZrO_2–Al_2O_3 composite materials are concerned, it would be a great advantage to manufacturers if the outstanding mechanical properties could be achieved without hot isostatic pressing. To this end future work needs to be carried out on the controlled sintering of these materials.

5 Ce–TZP

When the cost of TZP powder is taken into consideration the benefits afforded by replacing yttria with a cheaper stabilising agent become apparent. To this end an increasing amount of work is being undertaken in the ZrO_2–CeO_2 system.[45–47]

Coyle *et al.*[46] were among the first researchers to study TZP produced using the ZrO_2–CeO_2 system. They worked in the compositional range ZrO_2 10 to 20 mol% CeO_2 and were able to sinter materials to a high density in air. The grain sizes ranged from 2 to 30 μm. The low ceria content materials were monophase tetragonal but as the ceria content was increased two phase mixtures of tetragonal and cubic were produced. Strengths greater than 500 MPa and toughness greater than 6 MPa m$^{1/2}$ were achieved.

A more complete study of the mechanical properties over the tetragonal phase solid solution range was carried out by Tsukuma and Shimada.[47] Chemically homogeneous powders were sintered to more than 99% theoretical density in the temperature range 1400 to 1600°C. 12·2Ce–TZP had a grain size of 0·5, 1 and 2·5 μm after firing at 1400, 1500 and 1600°C, respectively. The shape and size of the grains were invariant in the compositional range 7 to 16 mol% CeO_2.

The amount of monoclinic formed on the fracture surface due to the stress-induced transformation was again found to be dependent on grain size and stabiliser content. The extent of transformation during fracture was considerable at grain sizes greater than 0·5 μm and ceria contents less than 10 mol% CeO_2. The trend in fracture toughness measured by the indentation technique correlated well with the extent of transformation on fracture (Fig. 22). It is also worth noting that in general the toughness of Ce–TZP can be considerably higher than Y–TZP.

The bend strength results shown in Fig. 23 do not show the expected correlation with the indentation fracture toughness results. The highest strengths were achieved in the compositional range 10 to 12 mol% CeO_2 when the grain size is less than 1 μm. The maximum value was 800 MPa which is much lower than the maximum strength achieved with Y–TZP.

The reason for the moderate strength of high toughness Ce–TZP may well be concerned with the mechanism responsible for the inelastic behaviour of this ceramic alloy.[47] Stress-induced transformation and microcracking on the tensile surface, prior to fracture, has been shown to be responsible for similar behaviour in high toughness Mg–PSZ.[48] The microcracks thus formed on the tensile surface propagate in a stable manner to form a critical flaw in conjunction with a critical member of the pre-existing flaw population and failure occurs at moderate stresses.

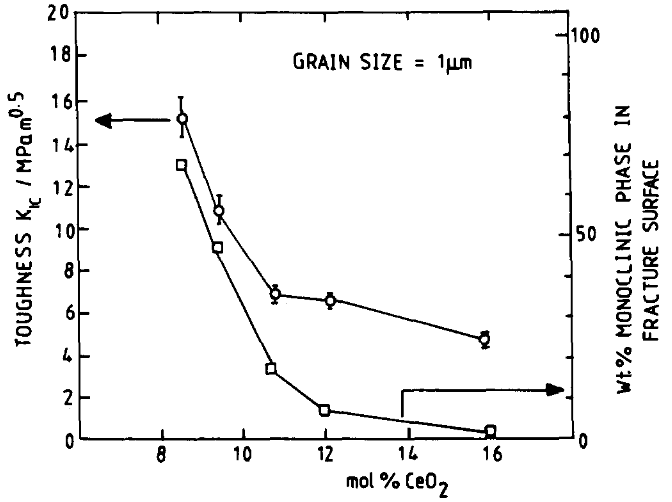


Fig. 22. Fracture toughness and monoclinic phase fraction on fracture versus ceria content of Ce–TZP.[47]

Similar behaviour may be responsible for the moderate strength of high toughness Ce–TZP.

Sato and Shimada[49] have also studied the low-temperature ageing behaviour of Ce–TZP in the compositional range ZrO_2 8 to 12 mol% CeO_2. They suspected that the low transformation temperature in the ZrO_2–CeO_2 system would give better thermal stability than materials in the ZrO_2–Y_2O_3 system. Chemically homogeneous powders were sintered in the 1400 to 1600°C temperature range.

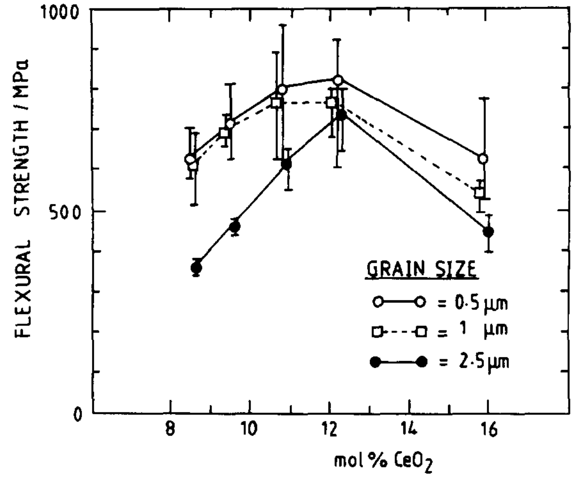


Fig. 23. Bend strength versus ceria content of Ce–TZP.[47]

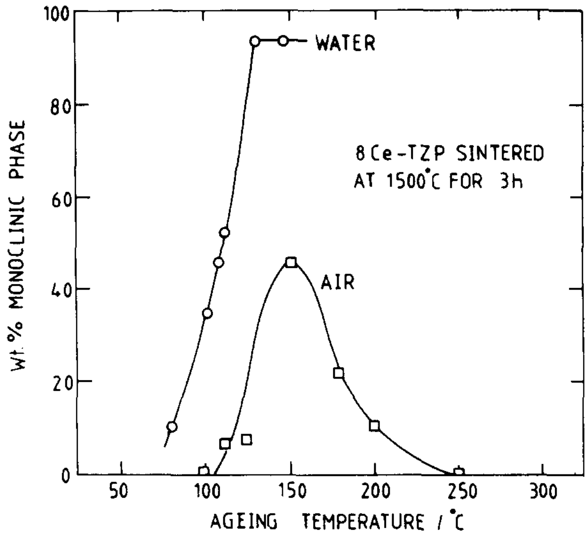


Fig. 24. Amount of monoclinic ZrO_2 formed on surface after annealing in air and water for 360 h.[49]

Low temperature annealing tests were then carried out in water and in air. The results in Fig. 24 show a similarity with Y–TZP materials in that the surface transformation was exacerbated by immersion in water during ageing.

Annealing in water produced almost full surface transformation after ageing at temperatures as low as 100°C. The rate of transformation during annealing in air was much slower and the maximum surface monoclinic

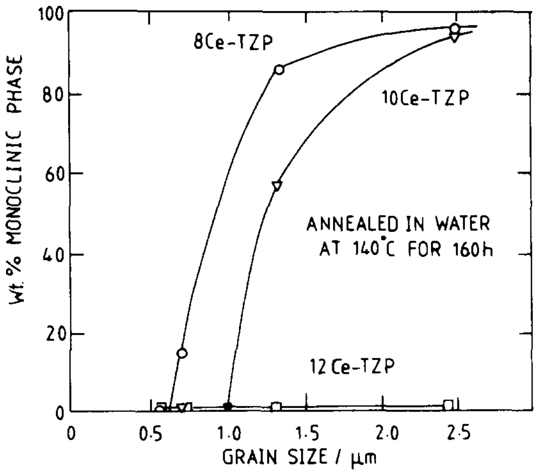


Fig. 25. Grain size dependence of monoclinic fraction after annealing in water at 140°C for 160 h.[49]

content was observed after ageing at 150°C, 50°C lower than for Y–TZP. In other respects the annealing behaviour is very similar to that of Y–TZP.

The grain size dependence of the surface transformation for 8Ce–TZP, 10Ce–TZP and 12Ce–TZP samples aged in water is shown in Fig. 25. As with Y–TZP, the amount of surface transformation increases with increasing grain size and decreases with increasing ceria content. For 12Ce–TZP no surface transformation was observed on ageing up to 160 h. The critical grain size below which no surface transformation was observed in the compositional range 8 to 12 mol% CeO_2 is approximately 0·7 to 1 μm; this is much larger than the equivalent critical grain size for Y–TZP.

6 CONCLUSION

Much of the early work on TZP was carried out in the ZrO_2–Y_2O_3 system since it offers the dual advantages of a low eutectoid temperature and an extensive range of solid solubility of yttria in tetragonal zirconia. It quickly became apparent that varying the sintering conditions and yttria content could have a dramatic influence on the mechanical properties. The trends in mechanical properties could be readily explained in terms of a critical grain size for spontaneous and stress-induced transformations. The results were consistent with the transformation toughening phenomenon, as was the increase in critical particle size with increasing yttria content. The optimum composition and sintering conditions have been defined and materials with excellent room-temperature mechanical properties fabricated. The relationship between mechanical properties and transformation toughening theory for Ce–TZP is less clear, especially since this ceramic appears to have high toughness but low strength. Surprisingly, the strength results do not correlate with the fracture toughness variation measured on Ce–TZP. Further work is required in the ZrO_2–CeO_2 system in order to produce a cheaper source of powder and so the incentive to match the properties of Y–TZP is high.

A systematic study of the effects of chemical homogeneity of the powder on TZP properties has yet to be undertaken. However, it is well documented that due to the slow interdiffusion in the ZrO_2–Y_2O_3 system, powder chemical homogeneity has a pronounced effect on the spatial distribution of yttria in the sintered product. The spatial distribution of yttria affects all the properties of Y–TZP and thus it is crucially important to have chemically homogeneous powders if optimum properties are to be attained.

Because of the superior mechanical properties of Y–TZP there has been much speculation about their possible use in automotive and other engineering applications. Unfortunately the degradation of mechanical properties of Y–TZP in the temperature range 20 to 1000°C, especially in moist atmospheres at 100 to 300°C, may well inhibit this application. Much work has been done to investigate this phenomenon but the underlying reason for surface destabilisation is yet to be clearly understood. Work has been directed to controlling the surface transformation by developing new materials or increasing the stabiliser content. A notable advance has been made with Y–TZP–Al_2O_3 composites, typically containing 20 wt% Al_2O_3. These materials have excellent room temperature and high temperature properties and are resistant to low-temperature ageing. However, hot isostatic pressing is required to develop the optimum properties in these materials and more work is required to achieve similar results by controlled sintering. If this becomes possible then volume production of engineering components may become more likely.

Recently an increasing amount of work has taken place in the ZrO_2–CeO_2 system to produce Ce–TZP material with comparable properties to Y–TZP. The motivation is to reduce the price of the powder by replacing yttria with a less expensive stabiliser. Ce–TZP materials show distinct promise and they exhibit superior toughness to Y–TZP. Unfortunately the strength of Ce–TZP is comparatively low and will require improvement before Ce–TZP presents a serious challenge to Y–TZP.

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