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Transformation strengthening of as-fired zirconia ceramics

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Abstract

The as-fired flexural strength of an Y_2O_3-doped ZrO_2 ceramics was evaluated by heat-treating the sintered ceramics in powder beds containing various fractions of the unstabilised, pure ZrO_2 powders for varying holding times. The annealing induced the tetragonal to monoclinic phase transformation near the surface, leading to a surface compression. Increase of the strength by 27% was obtained after 1 h annealing within the pure ZrO_2 powders. A concurrent enhancement on the Weibull modulus of the as-fired ceramics was also attained. These improvements implied that the strength-limiting flaws are probably controlled by the surface defects. Extending the annealing time did not further improve the strength. Microstructural analyses revealed that the removed yttria reacted with the packing powders to form a thin layer of rod-shaped grains as the annealing time was lengthened. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

1. Introduction

A recurrent interest in improving the as-fired strength of sintered ceramics has gained increasing attention in recent years [1]. The motivation ties in the fact that in order for ceramics to compete with the metal counterparts in the load-bearing applications, the fabrication cost of the ceramic parts has to be reduced. The machining cost, in particular, often represents more than half of the overall production cost for most structural ceramics. Therefore, if the as-fired strength of ceramics can be improved to a competent level with a satisfactory reproducibility, component designers can use the as-fired surface instead of the machined surface in places that the external loading and the dimensional tolerance of products are less strict.

Problems limiting the use of the as-fired surface are many, e.g. poor strength and reliability, faulty precision in dimensional variations, etc. In particular, the as-fired strength is often substantially inferior to that of the machined surface, and is susceptible to various process parameters, leading to an inconsistent reproducibility. It has been reported that the occurrence of subsurface voids was related to the sintering process [2], and the existence of the void was detrimental to the as-fired strength. Similar results on reduction of the void fraction was also attained by embedding the ceramics into powder beds, indicating that the environmental control during sintering was vital [3]. The strength-limiting flaws influencing the flexural properties may hence be categorised into at least two types, i.e. defects within the sintered compacts (including near surface defects not connecting to the surface) and surface flaws which are sensitive to process variables.

The transformation-toughened zirconia in either monolithic or composite form provides an interesting means in strengthening the as- fired properties. Because mechanical stresses can be produced by the molar volume change associated with the tetragonal-to-monoclinic phase transformation [4–6], Green first suggested that the transformation can be induced near the free surface by diffusing the stabiliser (e.g. yttrium oxide) out from the sintered compacts through a post-sintering annealing treatment [7]. The transformation introduces a surface compression; therefore, the applied external stress must first overcome the compressive residual stress before crack propagation [8,9]. The induced stress was thought to enhance the as-fired properties; therefore, this paper investigated the varying annealing treatments on the as-fired microstructure, phase composition and strength of the yttria-stabilised zirconia (Y-TZP) ceramics.

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Table 1
Characteristics of the ZrO_2 powders used in the experiment

Powder Characteristics	HSY-3.0 ZrO_2		SPZ ZrO_2	
Chemical composition				
	$ZrO_2 + HfO_2$	94.12%	ZrO_2	99.63%
	Y_2O_2	5.37%	TiO_2	0.15%
	Na_2O	0.01%	SiO_2	0.05%
	CaO	0.01%	CaO	0.05%
	L.O.I.[a]	0.08%	L.O.I.[a]	0.12%
Specific surface area	6.9 m^2/g		5.5 m^2/g	
Average particle size	0.25 μm		1.4 μm	

[a] Loss on ignition.

2. Experimental procedure

The zirconia powder (HSY-3.0, Daiichi Kigenso Kagaku, Japan) containing 3 mol% yttrium oxide (or equivalently, 5.3 wt%) as a stabiliser was used for the study. Characteristics of the ceramic powders are shown in Table 1. Bar-shaped samples were prepared by an injection moulding, followed by a thermal debinding at 600°C, and sintered at 1550°C with 1 h isothermal holding [10]. All the samples showed a sintered density exceeding 6.0 $g\,cm^{-3}$. Some of the samples were then annealed in powder beds containing mixtures of various fractions of the unstabilised, pure zirconia powders (SPZ grade, Daiichi Kigenso Kagaku, Japan) and the yttria-doped HSY-3.0 powders. The powder mixtures for the powder beds were prepared by homogeneously ball-mixing the weighted powders in alcohol media, dried and pulverised for later annealing treatment. The annealing treatment was conducted at 1400°C in air with various holding times.

The annealed samples were easily removed from the packing powders after the heat treatment, and the details of surface topography were examined by scanning electron microscopy (Cambridge Instrument, S360). The grain size was directly measured from the micrographs by using the line-interception method. At least 600 grains were measured for each sample and no attempts were made for the stereological correction of the two-dimensional images. The phase analyses were conducted by the X-ray diffractometry (MAC Science, M18X-1180, Japan) using the Cu K_α radiation at $\lambda = 0.15405$ nm. At least three measurements were performed for each identical processing condition to verify the reproducibility.

The flexural strength of the sintered samples was determined from the four-point bend test with a sample dimension of 3×4×48 mm. The specimens were placed so that the as-fired surfaces were subjected to the tensile stress of bending. The inner and outer span distances were 10 and 30 mm, respectively. The cross-head speed was held at 0.5 $mm\,min^{-1}$. Over 20 samples were tested to find an average strength for each processing condition.

3. Results and discussion

3.1. The as-fired microstructure

As shown in Fig. 1, a bimodal distribution of the zirconia grains (mixed grain size of average 0.54 ± 0.18 μm for the small-sized grains and 2.84 ± 0.78 μm for the large-sized grains) was observed for the ZrO_2 sintered at 1550°C for 1 h holding (referred to as the untreated ZrO_2). Air-annealing the untreated ZrO_2 at 1400°C for

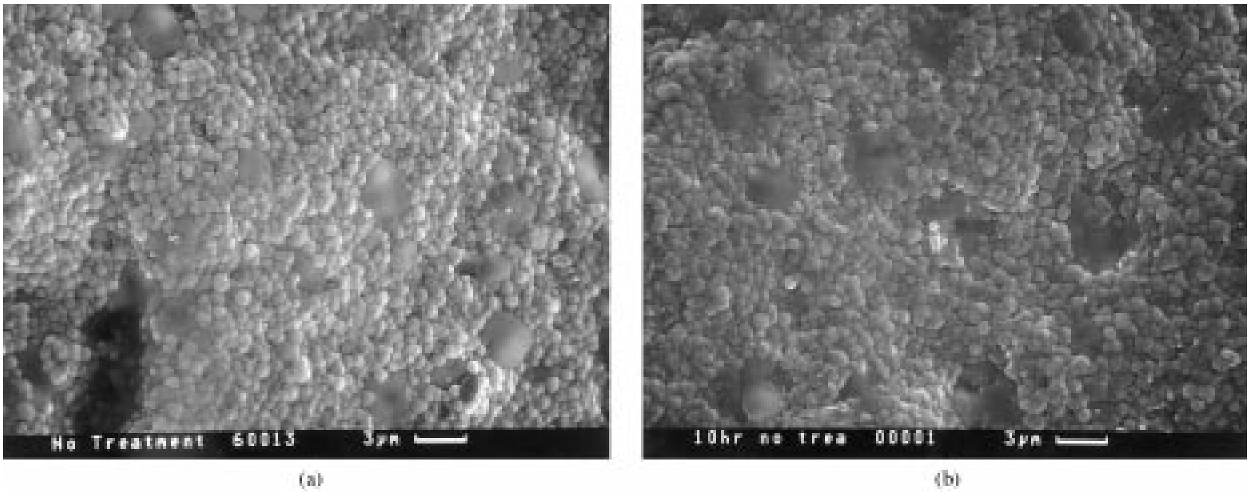

Fig. 1. The as-fired microstructure of (a) the untreated ZrO_2, and (b) the sintered zirconia annealed in air at 1400°C for 10 h.

10 h (referred to as the air-annealed ZrO_2) yielded similar average grain sizes of $0.62 \pm 0.20\,\mu m$ and $3.25 \pm 0.89\,\mu m$ for the small and large size grains, respectively. Therefore, the grain size of the sintered zirconia is relatively insensitive to the isothermal holding time of the air-annealing treatment.

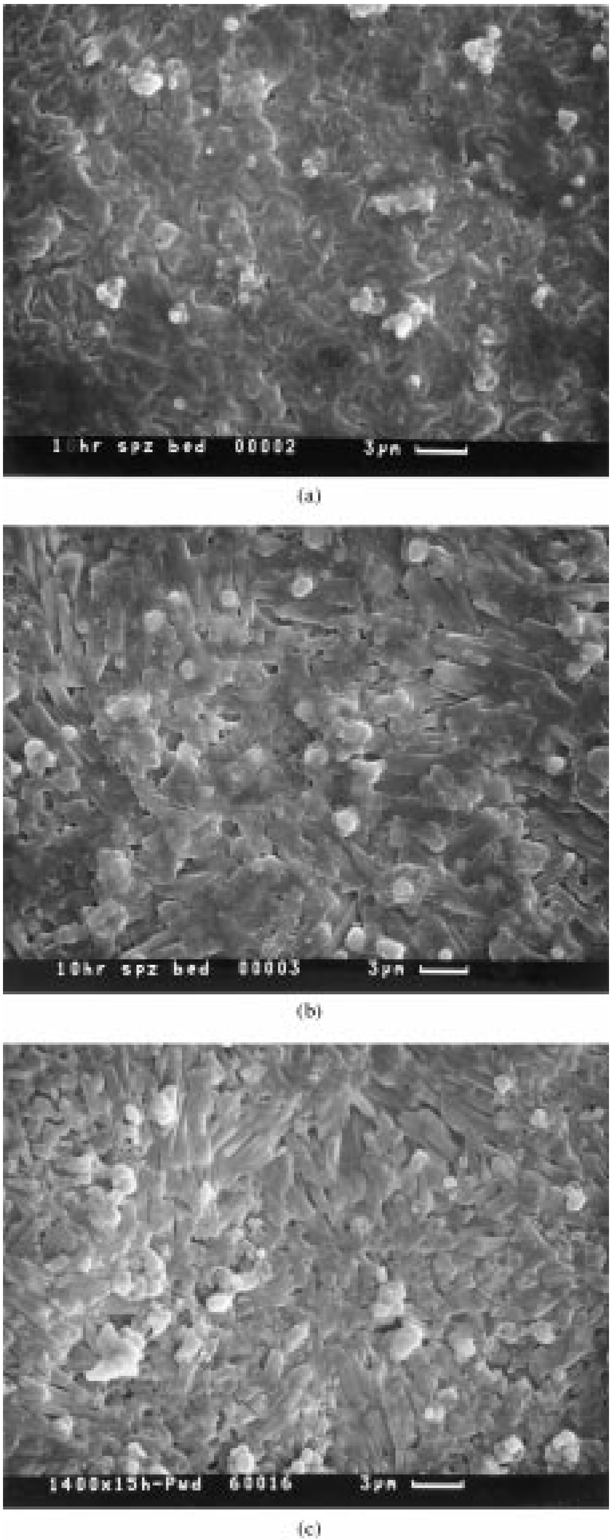

Fig. 2. The as-fired microstructure of the powder-bed annealed ZrO_2 with heat-treatment conditions of (a) 1-h, (b) 10-h and, (c) 15-h isothermal holding at 1400°C.

The annealed specimens embedded in the powder bed consisted entirely of the unstabilised SPZ powders during the annealing at 1400°C for various holding times (referred to as the powder-bed annealed ZrO_2), however, showed a distinctively different morphology. As shown in Fig. 2, reactions between the sintered surfaces and the packing powders seemed to take place during the annealing. The zirconia grains changed from the "partially coagulated" morphology to the rod-shaped grains as the annealing time was extended. These morphologies were seen all over the as-fired surfaces and not restricted in particular locations. Examining the morphology of the packing powders alone showed no apparent change in the particle shape after the annealing. In addition, the rod-shaped grains were also observed when immersing the sintered samples of a polished surface into the unstabilised SPZ powders for the same annealing treatment of 10 h. The microstructure in cross-sectional view revealed that the rod-shaped grains exist only in regions about 2 to $6\,\mu m$ from the surface. Therefore, we have suspected that the yttria removed from the sample might react with the adjacent packing powders to form a "layer" of new compound which exhibits a preferential grain growth as the annealing time lengthens. Further details regarding this presumption will be described in latter X-ray analyses.

3.2. Phase analysis

Typical diffraction patterns of the untreated, the air-annealed, and the powder-bed annealed ZrO_2 are shown in Fig. 3. The specimens without the heat treatment were mostly composed of the tetragonal phase, with remaining minor fraction of the monoclinic phase. The air-annealed ZrO_2 yielded no apparent change in the phase composition. Ruiz and Ready [11] reported that the tetragonal ZrO_2 transforms to the monoclinic phase during sample cooling if the grain size is larger than a critical size of about 5 to $6\,\mu m$. Therefore, the monoclinic phase in the untreated and the air-annealed samples may be resulted from the large-sized grains evidenced in Fig. 1.

The predominant composition changes from the tetragonal ZrO_2 to monoclinic ZrO_2 after the powder-bed annealing in the unstabilised SPZ powders. Increase of the annealing time from 1 to 10 h significantly reduces the tetragonal fraction; however, virtually indistinguishable phase intensity is seen when extending the annealing time to 15 h. The exodus of the stabiliser near surface is the main reason for the induced phase transformation [7–9].

A diffraction peak at about $2\theta = 25.8^{o}$ was also observed (Fig. 3). The intensity increased notably as the annealing time increased from 1 to 10 h. Attempts on identifying the composition suggested that the peak probably comes from yttrium-containing oxides, even though the exact composition was not successfully identified. The elongated grains on surface is believed to be associated with the formation of the yttrium compound since a substantial increase in peak intensity is observed when a notable grain growth is concurrently in operation.

3.3. As-fired flexural strength

The powder-bed annealed ZrO_2 generally exhibited greater strength in comparison with the untreated samples. As shown in Fig. 4, a substantial improvement is seen as the fraction of the unstabilised SPZ ZrO_2 exceeding over 70 wt% of the overall packing-powder mixtures. The strength reaches a maximum when the powder bed is composed solely by the unstabilised, pure SPZ powders. Fig. 5 shows the relation of the flexural strength to the various annealing times for specimens treated in the unstabilised SPZ powder beds at 1400°C. The average as-fired strength changed from 582.6 ± 84.8 MPa of the untreated samples to 740.2 ± 77.2 MPa of the 1 h annealed specimens. Extending the annealing time up to 15 h did not improve the strength any further; instead, a slight decrease in strength was observed. The formation of the thin yttrium-containing compound near surface may be the main cause for the strength reduction. The as-fired flexural strength of the air-annealed samples (1400°C for 10 h) was also measured for comparison reasons, and a mean strength of 599.3 ± 81.5 MPa was obtained, similar to that of the untreated sample. The strength increase was reported to be proportional to the difference in the fraction of the monoclinic ZrO_2 between the surface and the bulk [8,9].

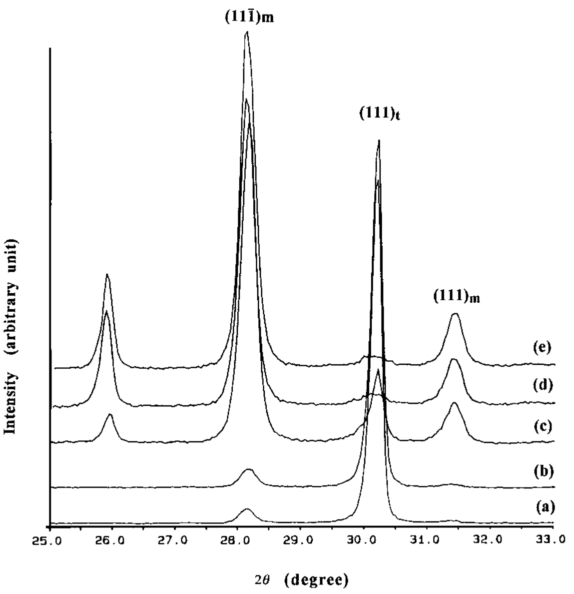

Fig. 3. The XRD diffraction patterns of (a) the untreated ZrO_2, (b) the air-annealed ZrO_2 and the powder-bed annealed ZrO_2 with (c) 1-h, (d) 10-h and (e) 15-h isothermal holding at 1400°C.

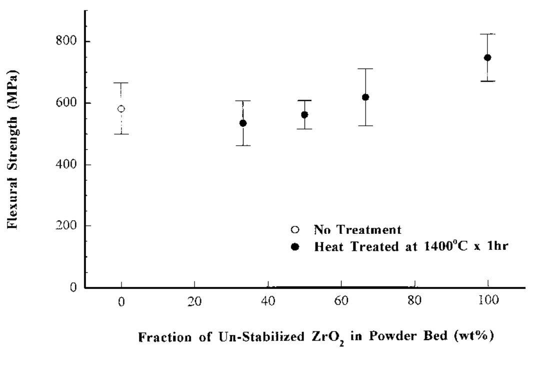

Fig. 4. The relations of the as-fired strength to varying packing powder compositions at the annealing temperature of 1400°C with 1-h isothermal holding.

The strength increase with the relatively short annealing time suggests that the as-fired properties are dominated by the surface and near surface flaws, particularly the surface flaw. By assuming that the as-fired strength is determined by the surface defect and the material is loaded under bending stresses, we may hence consider a surface defect presenting a crack length a intersecting the surface as shown in Fig. 6 (note that $h/2$ in the figure is the half-thickness of the sample bars). The bend strength σ_f is controlled by the surface flaw a and the intrinsic toughness K_{IC} of the substrate, and is given by [12]

$$\sigma_f = \frac{K_{IC}}{\sqrt{\pi a} Y} \quad (1)$$

with the dimensionless parameter Y depending on the geometry of the specimen and the crack. Note that $0.982 < Y < 1.122$ for $a/h < 0.1$ (or in the case of 3 mm-thick bend bars, $a < 300$ µm). It can be seen from Eq. (1) that the flexural strength is inversely proportional to the square root of the crack length of the

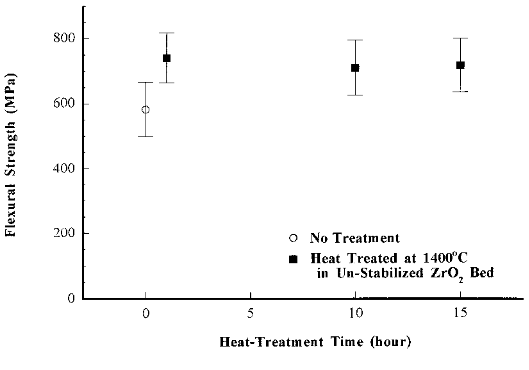

Fig. 5. The as-fired strength of the powder-bed annealed ZrO_2 at various annealing times.

as-fired surface flaws. The compressive residual stress associated with the tetragonal to the monoclinic ZrO_2 transformation on surface may be conceptualised in such a way that the physical significance of the actual crack length on surface is reduced, i.e. the surface with a crack length a is then reduced to an effective length a' in the case that the surface compression exists. Since the crack-length population of the untreated and the powder-bed annealed samples may be treated identical, the ratio of the crack length for samples with and without the phase transformation may hence be given by

$$\frac{\sigma_f}{\sigma_f'} = \sqrt{\frac{a'}{a}} \qquad (2)$$

where σ_f' and a' are the bend strength and the "effective" crack length of the powder-bed annealed samples, respectively. We may thus find that the surface crack length reduces to 62% of their actual size as the annealing (1400°C for 1 h in the powder bed) was applied; or equivalently, the nominal crack size diminished from a range of $47.6 < a < 62.2$ μm to $29.5 < a' < 38.6$ μm after the annealing treatment.

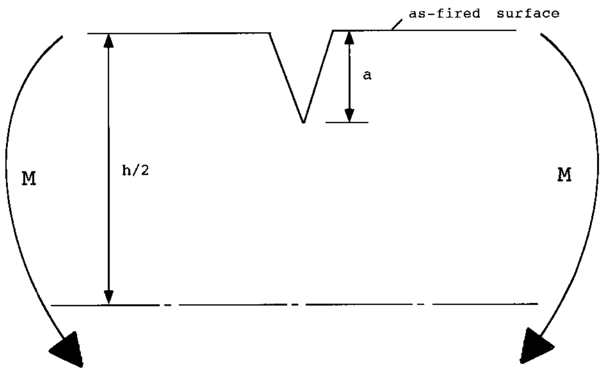

Fig. 6. A schematic plot showing a surface crack on the as-fired surface under a bending tension.

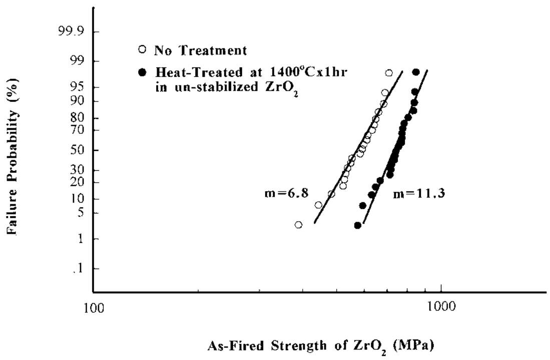

Fig. 7. The Weibull moduli of the untreated and the powder-bed annealed ZrO_2 ceramics.

3.4. Weibull modulus

The powder-bed annealing not only improved the strength, but also significantly improved the flaw tolerance of the sintered zirconia. A substantial increase in the Weibull modulus from 6.8 to 11.3, a 66% increase, was found (Fig. 7). The concept of the effective crack length may be applied to explain the Weibull enhancement. Since the strength-determining flaws near the surface reduce their effective length after the annealing, we would hence expect the flaw population moving toward a smaller flaw size, which would then lead to an improved Weibull modulus accordingly.

4. Conclusion

Considerable improvements on the strength and Weibull modulus of the as-fired zirconia are obtained by annealing the sintered samples in the unstabilised zirconia powder bed. The strength increase is resulted from the phase transformation induced on the surface due to the diffusion of the stabiliser from samples to the powder bed. In particular, the strength enhancement is attained within a short annealing time, suggesting that the strength is dominated by the surface flaws. Examination of the surface microstructure revealed that reactions occurred between the packing powder and the sintered zirconia surface. The grain morphology changes from the spherical to rod-shaped grains as the annealing time increases. Formation of the yttrium-containing compound is found to hinder further strength increase as the annealing time prolongs. Accompanying with the strength improvement, a substantial increase in the Weibull modulus was also observed. The enhancement in the as-fired properties is interpreted as a reduction in the effective crack length of the surface flaws by the induced phase transformation.

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